Aspects of Self-Propulsion

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A Dissertation Submitted to
Indian Institute of Technology Hyderabad
In Partial Fulfilment of the Requirements for
The Degree of Master of Science

Department of Physics

April 2013

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Acknowledgements

I would like to thank my supervisor Dr. Debasish Chaudhuri for his guidance and his support. I would also like to thank our Head of Department, Dr.Anjan Giri and the faculty members of the Physics department for giving me an opportunity to work on a project as part of my curriculum and also listening to me talk about my work, and offering support and encouragement whenever I needed it.

Dedication

I would like to dedicate this thesis to my family.

Aspects of Self Propulsion

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Fluctuating thermodynamics of Active Brownian Particles

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arXiv:1304.7138
Submitted to Physical Review E

Abstract

We present a formulation by which the fluctuating thermodynamics for the case of self propelled particles can be calculated. We identify the first law of thermodynamics from the context of energy conservation. Using the Detailed Fluctuation Theorem, we arrive at a definition of entropy.We apply this formalism to the Rayleigh Helmholtz and Energy Depot models of self propulsion. The formalism is extended to higher, namely two dimensions. In the last section, the possibility of phase coexistence in the many body problem of interacting self propelled particles and passive particles in an external harmonic trap is examined.

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Chapter 1

Self Propelled systems and Collective motion

1.1 Introduction

In nature around us, displays of patterns formed by living units are abundant. A school of fish that move in an ordered manner swirls like a violently stirred fluid in the presence of a predator. Birds such as starlings fly in well defined patterns in the sky but when they return to their roosting site they lose this order and form turbulent patterns. The common feature among all these situations is the presence of living things as the units of this collective pattern formation. Persistent motion or self propulsion is one of the basic characteristics of life. However experimentally several non living things can be made to have these characteristics of self propulsion as has been demonstrated.

Most of these systems are non equilibrium systems. There exists a class of biological and physical systems that are referred to as active matter. These systems are characterized by their ability to move due to some internal driving mechanism. This driving mechanism can be chemical reactions as in the case of living systems, or it can also be due to some non equilibrium dynamics, as in the case of artificially driven systems. Thus this type of motion differs from the usual passive motion of molecules in liquids and gases, in the fact that there exists an internal motor which takes in energy from an external source and transforms it under non equilibrium conditions to directed accelerated motion. This active motion can be attributed to either an internal energy depot or a non-linear velocity dependent friction function.

Another important feature of active matter systems is the present of non-negligible random fluctuations in the motion of each unit. This is because of the smallness of the constituents of each individual unit. This so called 'noise' which appears in the dynamics may be due to fluctuations in the environment or also in the internal processes generating this active motion.Whatever be its source, it is usually modelled, without taking into consideration its underlying mechanism, by means of a stochastic force introduced into the equations of motion. The properties of this stochastic force is that the time scales in which this force can fluctuate is much smaller than the time scales in which the dynamical observables of the system in question, change. Along with the presence of a viscous force,this has the characteristics of a Brownian particle which is undergoing active motion. Thus most self propelled systems can be modelled using the concept of an Active Brownian Particle.

Active Brownian particles also show the property of collective motion as has already been described. This is typically observed in systems that have a large number of interacting similar

units. These interactions may be simple, such as attraction or repulsion, or it may be complex as a combination of several simple interactions, and can occur between neighbours in space or on an underlying network. Sometimes transitions may occur and the units may adopt a form of behaviour which is completely determined by the presence of the other units in the system. The reason why questions of whether these patterns are system specific or whether they can be classified into well defined groups, is interesting from a physical point of view is that, analogies can be drawn between these biological systems and the systems that are studied in statistical physics.For example the renormalizaion theory proposed by Wilson in 1975 proposed that the main features of transitions in an equilibrium system are insensitive to the details of the interaction between the units of that system. Thus it is considered that the orientational forces between atoms can result in ordering phenomena which are observed in collectively moving systems of living organisms.

However the main point of difference between collective phenomena in physical and biological systems is the so called 'collision rule' which states how the velocities of the units evolve during interaction. In the case of biological systems it does not preserve the momentum. In physically closed equilibrium systems by Newtonian dynamics we obtain the familiar Maxwellian distribution of velocities which conserve momentum. However the requirement of maintaining a constant velocity despite the presence of interaction between the units can be realized only in the case of open systems. Currents are generated and the system becomes non-equilibrium in nature. The initial state of the system is considered to be random and hence possessed of very little momentum, which however increases due to the presence of non-zero currents in the system. Ordering occurs, provided that the random fluctuations against ordering are small enough.[1, 2, 3, 4, 5, 6, 8, 7]

1.2 Observations and Experiments

The list of systems which display collective behaviour is vast. I shall, hence describe only a few such examples. As I have already mentioned, the size of the particle is important in determining the forces that play a significant role. For example, particles as small as molecular motors experience a significant random force caused due to the collisions it undergoes with the molecules of the fluid. Thus they behave like a Brownian particle with a self propulsion mechanism, leading them to be described as active Brownian particles. In entities which are too large to experience this random Brownian force that is often called *noise*, this fluctuation in the equations of motion can be attributed to other causes. For example, in animals the noise in the trajectory of the animal can arise from random decision making processes.



Figure 1.1: Examples of collective motion

1.2.1 Self propelled systems that are affected by the random Brownian noise

Collective motion is also observed in bacterial colonies which are grown on agar surfaces. A certain kind of bacterium, for example, called Bacillus subtilus when closely packed forms a certain kind of ordered phase called 'Zooming Bio Nematics' (ZBN) (Cisneros *et al.*, 2007).

Experimentally, the simplest realization of a self propelled particle was reported by Ibele *et al*,(2009).who described silver chloride particles which execute collective motion in deionized water under UV illumination. Other examples of experimental setups to model SPPs are conducted on rods placed on a vibrating table, both apolar and polar, Blair *et al.*, (2003) and Kudrolli *et al.* (2008). Vortex patterns were observed which nucleate and grow as a function of time for the apolar case and clustering behaviour was observed for the polar case. Experimental results have suggested that only a few parameters govern the phenomenon of collective motion. One of these factors was found to be particle density. Several experiments on biomolecules have confirmed this fact. In these experiments, actin filaments and fluorescently labelled reporter filaments are propelled by randomly oriented molecular motors (myosin molecules) which are immobilised and attached to a planar surface. Butt *et al.*(2010)observed that for higher densities the sliding movement of these actin filaments show bulk alignment despite the fact that the myosin molecules are randomly oriented.

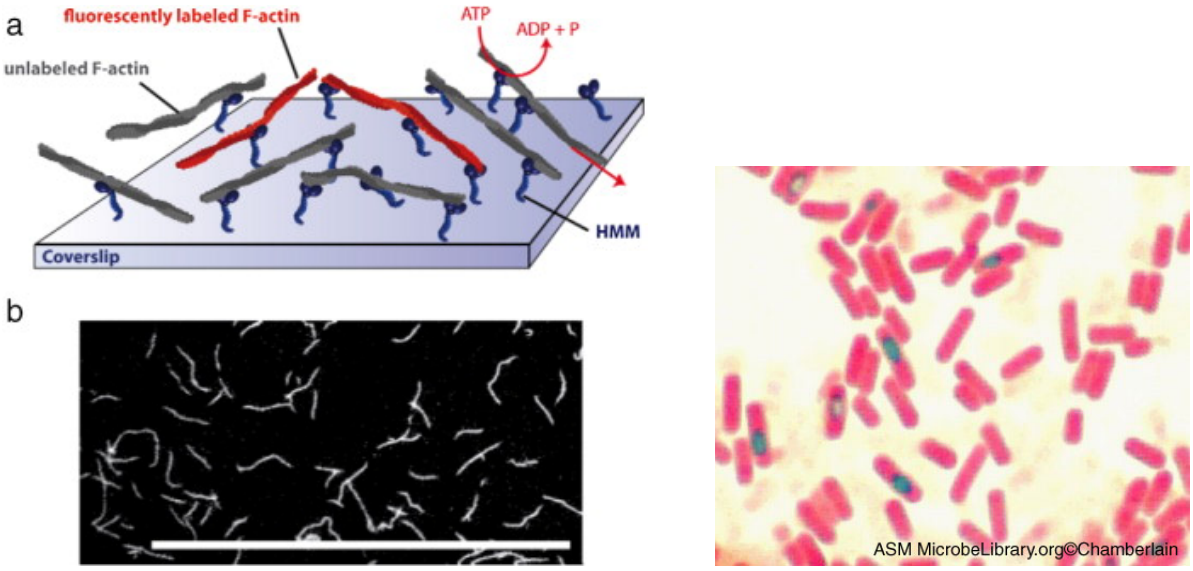


Figure 1.2: These systems are small enough to experience the random fluctuating force

1.2.2 Self propelled systems that are too large to be affected by the random Brownian noise

Systems exhibiting such collective motion include flocks of birds, school of fishes, crowds of people, and even systems in a microscopic level such as kinesin motors carrying a single cargo in the microtubule track inside a cell.Fish schools and shoals, though referring to a collection of fish are not synonymous. Schools are more tightly organised in momentum and direction and less prone to predator attacks than shoals. Becco et al., (2006)recorded trajectories of young fish in a school. Individual and collective behaviour was studied as a function of fish density and a transition from disordered to correlated motion was found. In the case of birds as well, Cavagna *et al.*, (2010) obtained high resolution spatial data of thousands of starlings using stereo imaging in order to calculate the response of a large flock to an external perturbation.

Insects also exhibit collective motion. In the case of social insects such as ants, termites or bees, their flocking characteristics are also governed by other more complex principles. In general an aggregation of insects is formed when it is advantageous for the group in the sense of providing more information, protection, choice of mates at the cost of limited resources and increased probability of various infections. However recent studies have demonstrated that the depletion of nutrition among certain insect species may lead to cannibalism among its group members. For example Bazazi *et al.*, (2008) showed that mass migration was strongly influenced by cannibalistic interactions among juvenile desert locusts.

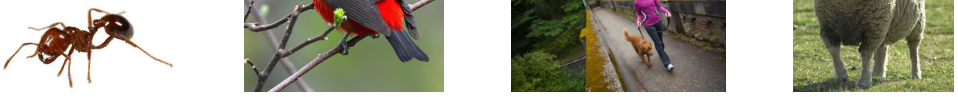


Figure 1.3: These systems are too large to be called Brownian

Chapter 2

Random motion, Diffusion and Brownian Motion

One of the simplest non-equilibrium systems is the diffusive system, the most famous experimental manifestation of which is Brownian motion.The random motion of a small particle immersed in a fluid is known as Brownian motion. The concept of Brownian motion has now not been restricted to a single particle but also to some collective property of a macroscopic system.This can be, for example the instantaneous concentration of a particular component of a system which is close to equilibrium.

2.1 Diffusion

The movement of molecules in the direction opposite to the concentration gradient has been generally observed in most cases. When this proceeds such that the equilibrium average of the squared displacement varies linearly with time, the system is said to be diffusive.

2.1.1 Fick's law

Let us consider particles of arbitrary nature that are dissolved in a fluid medium.If the total number of these particles $n(\mathbf{x}, t)$ does not change with time then we can write a continuity equation for density for these particles,

$$\frac{\partial n(\mathbf{x}, t)}{\partial t} + \nabla \mathbf{j}(\mathbf{x}, t) = 0 \tag{2.1}$$

where $\mathbf{j}(\mathbf{x}, t) = \sum_{\alpha} \mathbf{v}_{\alpha}(t)\delta(\mathbf{x}-\mathbf{x}_{\alpha})$ is the particle current and $\mathbf{v}_{\alpha}(t) = \dot{\mathbf{x}}_{\alpha}(t)$ is the particle velocity. In thermal equilibrium, there exists a uniform distribution of particles and the average $\langle \mathbf{n}(\mathbf{x}, t) \rangle$ remains independent of $\mathbf{x}$ and t. If however, the initial conditions of the system are prepared such that there exists a non-uniformity in the density, on removing the initial constraints that caused this, the system shall tend to the equilibrium uniform distribution. This will happen if the particles move which leads us to the conclusion that a non-uniform density will give rise to a non-zero current $\mathbf{j}(\mathbf{x}, t)$ in the system. If the spatial inhomogeneities in density are small then it is expected that the currents that are formed as a result of this are also small. Thus in this limit we can expect the current to be proportional to the gradient of the density,and as the current must transform as a vector, the relation that is simplest, is,

$$\mathbf{j} = -D\nabla \mathbf{n} \tag{2.2}$$

This is the Fick's law.It is a phenomenological relation. The coefficient D is known as the diffusion coefficient. The current is opposite in sign to the density gradient which indicates that

the particles move opposite to the density gradient, that is, from a region of higher concentration to a region of lower concentration. Thus the particle current tends to try to bring the system to the uniform density condition again.Another point to be noted is that under time reversal, the particle current changes sign while $n(\mathbf{x}, t)$ and its gradient are even. Thus time reversal symmetry is broken and the Diffusion coefficient can be interpreted as a sort of dissipation coefficient. On substituting Fick's law in the continuity equation (2.6) we get the Diffusion equation.

$$\frac{\partial n}{\partial t} = D\nabla^2 n \tag{2.3}$$

Assuming the trial solution to be as $n(\mathbf{x}, t) \sim e^{-i\omega t}$ we get the mode frequency to be

$$\omega = -iDq^2$$

where $q = 2\pi/\lambda$ is the wave number of the spatial modulation of the density. The frequency is purely imaginary implying that the response of $n(\mathbf{x}, t)$ to external forces or non-equilibrium conditions will decay exponentially to zero in times of the order of $D^{-1}\lambda^2$.There will be no oscillatory part of the decay.

2.1.2 The solution of the Diffusion equation: Green's function method

We can relate the particle number density $n(\mathbf{x'}, t')$ at a position $\mathbf{x'}$ and at a time t' to the particle number density at a position and time $\mathbf{x}$ and t by

$$n(\mathbf{x}, t) = \int d^d x' G(\mathbf{x} - \mathbf{x'}, t - t') n(\mathbf{x'}, t') \tag{2.4}$$

where $G(\mathbf{x} - \mathbf{x'}, t - t')$ is the diffusion Green's function satisfying the boundary condition that,

$$n(\mathbf{x}, t = 0) = \delta(\mathbf{x} - \mathbf{x'})$$

For times greater than $t = 0$ the Green's function satisfies the Diffusion equation,

$$\frac{\partial G(\mathbf{x}, t)}{\partial t} + D\nabla^2 G(\mathbf{x}, t) = 0$$

On performing a Fourier transform over the spatial coordinates and a Laplace transform over the time coordinates, we get,

$$G(\mathbf{q}, z) = \frac{1}{-iz + Dq^2} \tag{2.5}$$

We then perform an inverse Laplace transform on the Green's function,

$$G(\mathbf{q}, t) = \int_{-\infty+i\epsilon}^{+\infty+i\epsilon} \frac{dz}{2\pi} e^{-izt} G(\mathbf{q}, z) = e^{-Dq^2|t|} \tag{2.6}$$

This is followed by an inverse Fourier transform to obtain the Green's function as,

$$G(\mathbf{x}, t) = \int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q}.\mathbf{x}} G(\mathbf{q}, t) = \frac{1}{(4\pi D|t|)^{d/2}} e^{-|x|^2/(4D|t|)} \tag{2.7}$$

This says that the particle density is confined initially at the origin and spreads to a region at time t occupying a mean square radius, given by,

$$\langle |\mathbf{x}|^2 \rangle = 2dD|t| \tag{2.8}$$

where d is the dimension of the space considered.
This is the relation for the Diffusion coefficient as found by Einstein in the case of Brownian motion. Thus the Green's function relates the particle density at a particular position and time to the particle density at a different position and time.

2.2 Fick's law in the presence of external potentials: Einstein's relation

All the previous discussions considered systems which were not under the influence of any external potential. However when we consider an external field, for example a gravitational field, the particles begin to move under its influence and this sets up a drift in the system. Einstein in his paper on Brownian motion in 1905 particles in a very dilute suspension in the presence of a gravitational force. Thus the only two forces acting on the system, as the solution is too dilute to consider inter-particle interactions, are the gravitational force and the forces due to the collisions on each particle by the particles of the fluid. These collisional forces can be modelled in the form of a dissipative force, and these particles begin to drift under the action of the external potential. At steady state this dissipative force must balance the external forces. Assuming that these external forces are conservative, that is derivable from an $\mathbf{x}$ dependent potential, we have for the drift velocity,

$$\mathbf{v}_D = \frac{1}{\gamma}\mathcal{F}_{ext} = -\frac{1}{\gamma}\nabla U(\mathbf{x}) \tag{2.9}$$

where γ is the dissipation coefficient.The The total particle current now acquires a drift component, which can be written as $\mathbf{j}_{drift} = n\mathbf{v}_D$ in addition to having a diffusive component and can be written as,

$$\begin{aligned} \mathbf{j}_{total}(\mathbf{x},t) &= -D\nabla n + \mathbf{j}_{drift} \\ &= -D\nabla n - \frac{n}{\gamma}\nabla U(\mathbf{x}) \end{aligned} \tag{2.10}$$

At thermodynamic equilibrium the total current must be zero and thus by the Boltzmann distribution we have the mean particle number as

$$n \sim e^{-U(\mathbf{x})/K_BT}$$

Using this relation in equation (2.15) we get,

$$D = \frac{T}{\gamma} = \frac{T}{6\pi\eta a} \tag{2.11}$$

where the last equality was obtained from the Stoke's law, where a is the radius of the particle and η is the viscosity of the medium.This relation was first derived by Einstein in his original paper and is the first of the fluctuation dissipation relations.In one dimension,

$$\begin{aligned} D &= \frac{\langle|\mathbf{x}|^2\rangle}{2Dt} \\ &= \lim_{t\to\infty}\frac{\langle[\mathbf{x}(t)-\mathbf{x}(0)]^2\rangle}{2Dt} \end{aligned} \tag{2.12}$$

Thus the equation (2.11) expresses the equilibrium average shown above in terms of the dissipation coefficient γ.
The total current density $\mathbf{j}_{total}$ can be written as,

$$\mathbf{j}_{total} = -\gamma^{-1}n\nabla(T\ln n + U) \tag{2.13}$$

Other than the Boltzmann constant, $T\ln n$ is just the chemical potential $\mu(n) = \frac{\delta F}{\delta n}$ where F is the free energy of a system of non-interacting particles. The external potential U is the negative of the external chemical potential $\mu_{ext}(\mathbf{x})$ The total current can now be written as,

$$\mathbf{j}_{total} = -\Gamma(n)\nabla[\mu(n) - \mu_{ext}(\mathbf{x})] = -\Gamma(n)\nabla\left(\frac{\delta F_{total}}{\delta n}\right) \tag{2.14}$$

where $\Gamma(n) = (n/\gamma)$, which is a density dependent dissipation coefficient and $F_{total} = F[n(\mathbf{x})] - \int d^d x \mu_{ext}(\mathbf{x}) n(\mathbf{x})$. At equilibrium,

$$\mu_{ext} = \frac{\delta F}{\delta n}$$

and there is no current. Thus a current can only flow if there is a gradient in the chemical potential, or when $\mu_{ext}(\mathbf{x})$ differs from $\mu(n)$.
When $n(\mathbf{x}, t)$ differs from its equilibrium value n_{eq} by an amount $\delta n(\mathbf{x}, t) = n(\mathbf{x}, t) - n_{eq}$ we have a current flowing which, for small and slowly varying δn is given by,

$$\begin{aligned} \mathbf{j}_{total} &= -\Gamma(n)\nabla\left[\frac{\partial \mu}{\partial n}\delta n\right] \\ &= -\Gamma(n)\frac{\partial \mu}{\partial n}\nabla n(\mathbf{x}) \end{aligned} \tag{2.15}$$

where the spatial variations of $\frac{\partial \mu}{\partial n}$ are taken to be negligible.We can compare this equation with Fick's law,equation (2.7) and find an alternative expression for the diffusion coefficient,

$$D = \Gamma(n)\frac{\partial \mu}{\partial n} = \frac{\Gamma}{\chi} \tag{2.16}$$

where $\chi = (\partial n/\partial \mu)$. Although this expression for D was derived by assuming a dilute suspension with particles which are in effect, non-interacting, it is applicable for denser systems where particle interactions become significant. However Γ becomes a more complicated function of density and the chemical potential changes to accommodate the interaction.

2.3 Robert Brown and his mysterious moving particles

A British Botanist, Robert Brown had been working on experiments to describe the precise nature and structure of pollen. He used a simple microscope that had a lens with a focal length of 0.8 mm and had a magnification of approximately 400.He began his investigations on particles that are contained in the pollen of the plant *Clarkia pulchella*. These particles were not uniform in shape or size, but varied from oblong to spherical to cylindrical in shape. He aimed to investigate the mechanism of fertilisation by tracking the oblong shaped particles, which could easily be distinguished from the other particles. He was able to estimate the dimensions of these particles upto an accuracy of 1μm, which were of sizes ranging from 5 to 6 μm.He also observed that these particles were in a state of continuous seemingly random motion, and the form of the particles kept changing. After careful observation Brown concluded that the motion of the particles did not arise from currents in air or the fluid. Careful evaporation of the fluid also failed to affect these particles. Thus he concluded that the motion of the particles was intrinsic to them. He was convinced that this was an indication of the fact that these particles possessed life. Later studies on Brownian motion by Darwin revealed that smaller the size of the particles observed,the faster they could move.This in the light of the present theory of diffusion indicates that the viscous drag force varies inversely with the dimensions of the particle. Later in order to test his hypothesis about whether the random motion shown by pollen grains was indicative of life, Brown repeated his experiments, this time on Mosses and Equista which had dried for over one hundred years, and also on, gum resins, pit coals and even shards of broken glass. His results did not change except for the variation expected due to size and shape. He also established that external forces were not responsible for this motion of the particles but he was unable to come up with a satisfactory explanation for this,leading scientists at the time to remain unconvinced. It was the establishment of kinetic theory and Einstein's theory of diffusion that would finally lead to a satisfactory explanation of Brownian motion.

2.4 Einstein's explanation:The mystery is solved

Motion consisting of a sequence of discrete steps is known as random motion. The position $\mathbf{x}(y)$ is a random function of time. Such a variable is known as a random variable.The series of values of a stochastic variable is known as a stochastic process. Einstein used the concept of transition probabilities of these stochastic variables to solve this random walk problem. In 1905, Einstein published an article titled *Concerning the motion, as required by the molecular-kinetic theory of heat, of particles suspended in liquids at rest.* In his explanation of Brownian motion he made the following assertions.

- The motion is caused by the frequent collisions of the perpetually moving molecules of the liquid with the pollen grain.
- The motion of the molecules is complicated and its effect on the motion of the pollen grains can be described as very frequent, statistically independent impacts on the pollen.

The assumption underlying the above is that the collisions between any two particles, and the collisions occurring between two particles at different times, given that the time interval is large enough; are independent.
Thus he assumed that there are n particles suspended in the system. The x-coordinate of each particle undergoes an increment of δ at some later instant of time. The value of δ can be positive or negative, but its values must follow a probability distribution $\phi(\delta)$ which has the characteristics that $\phi(\delta) = \phi(-\delta)$ and $\int_{-\infty}^{\infty} \phi(\delta)d\delta = 1$. Thus the number of particles at time $t + \tau$ found between x and $x + dx$ is,

$$f(x, t + \tau)dx = dx \int_{-\infty}^{\infty} f(x + \delta, t)\phi(\delta)d\delta \tag{2.17}$$

This is known as the Chapman-Kolmogorov equation. In effect, it states that the probability of finding a particle at a position x at a time $t + \tau$ is the sum of the transition probabilities of particles at all possible positions $x + \delta$ to be pushed to the position x multiplied by the probability of being at the position $x + \delta$ in the first place. This assumption is Markovian as it is essential that the push δ is independent of the previous collisions undergone by the particle. Assuming that the time interval τ and the space interval δ are very small,we have

$$f(x,t)+\tau\frac{\partial f}{\partial t} = f(x,t)\int_{-\infty}^{\infty}\phi(\delta)d\delta+\frac{\partial f}{\partial x}\int_{-\infty}^{\infty}\delta\phi(\delta)d\delta+\frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{\infty}\frac{\delta^2}{2}\phi(\delta)d\delta+(\text{higher order terms}) \tag{2.18}$$

This is known as the Kramers-Moyal expansion. Using the properties of $\phi(\delta)$, and setting

$$\frac{1}{\tau}\int_{-\infty}^{\infty}\frac{\delta^2}{2}\phi(\delta)d\delta = D \tag{2.19}$$

where D is the equilibrium diffusion constant,
we get the Diffusion equation,

$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2} \tag{2.20}$$

This is in fact the Fokker Planck equation for the case of Markovian systems. The solution to this can be found using the boundary condition that $f(x, 0) = \delta(x)$ where $\delta(x)$ is the Dirac Delta function,

$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}}e^{-x^2/4Dt}$$

Einstein concluded by finding the root mean square displacement as

$$\langle\Delta x\rangle = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = 2Dt \tag{2.21}$$

This problem can also be approached by identifying the transition probability. Thus,in the dilute limit, the probability that the αth particle is at position $\mathbf{x}$ at time t after it was at position $\mathbf{x}_0$ at time t_0 is given by,

$$P(\mathbf{x}, t|\mathbf{x}_0^\alpha, t_0) = \langle \delta(\mathbf{x} - \mathbf{x}^\alpha(t)) \rangle_{\mathbf{x}_0^\alpha t_0} \tag{2.22}$$

where the average is taken over the random force that originates due to the collision with the fluid particles, and generates the instantaneous position of the particle $\mathbf{x}(t)$. The boundary condition that the particle was at $\mathbf{x}_0^\alpha$ when $t = t_0$ is implemented by the condition that $\mathbf{x}(t_0) = \mathbf{x}_0^\alpha$. The average density of the particles at time t given that the density of the particles at time $t = t_0$ was $n(\mathbf{x}, t_0) = \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_0^\alpha)$. is given by,

$$\begin{aligned} \langle n(\mathbf{x}, t) \rangle &= \langle \delta(\mathbf{x} - \mathbf{x}^\alpha(t)) \rangle_{\mathbf{x}_0^\alpha t_0} = \sum_\alpha P(\mathbf{x}, t|\mathbf{x}_0^\alpha, t_0) \\ &= \int d^d x_0 P(\mathbf{x}, t|\mathbf{x}_0, t_0) \sum_\alpha \delta(\mathbf{x}_0 - \mathbf{x}_0^\alpha) \\ &= \int d^d x_0 P(\mathbf{x}, t|\mathbf{x}_0, t_0) n(\mathbf{x}_0, t_0) \end{aligned} \tag{2.23}$$

This equation is identical to equation (2.4) and we can identify the transition probability $P(\mathbf{x}, t|\mathbf{x}_0, t_0)$ with the Green's function in the dilute limit.

$$P(\mathbf{x}, t|\mathbf{x}_0, t_0) = G(\mathbf{x} - \mathbf{x}_0, t - t_0)$$

Thus the mean square displacement of a single Brownian particle shall follow the equation (2.7) with $d = 3$ and with the diffusion constant taken from equation (2.11) which is appropriate for a non-interacting particle diffusing in a fluid with viscosity η, we get,

$$\langle (\Delta x)^2 \rangle = \langle [\mathbf{x}(t) - \mathbf{x}_0]^2 \rangle = 6Dt = \frac{K_B T}{\pi \eta a} t \tag{2.24}$$

This is the Einstein's relation for a diffusive system that has been obtained previously.The diffusion of the average density of particles as well as the diffusion of a single particle are in general two different processes and are controlled by two different diffusion coefficients. These only become equal when the particles are non-interacting, which is the assumption that has been used in the above derivation.

2.5 Perrin's experiment:Confirmation of Einstein's theory

Perrin,for his studies on Brownian motion received the Nobel prize in 1926 as he *'put a definite end to the long struggle regarding the real existence of molecules'*.During his studies on Brownian Motion he used colloids, most of which were emulsions. He was able to prepare an emulsion made of gamboge and mastic. These contained grains of various sizes. At this point Perrin realized that he needed uniform emulsions of equal sized grains for his measurements. He then used centrifugation to separate the equal sized grains from the unequal sized grains.

2.5.1 Determination of density and radius

Perrin determined the density and radius of the grains, each by three different methods. One measurement of density was done by the specific gravity bottle method.Water and emulsion were filled in the same bottle and their masses were determined. The suspended resin was dessicated in the oven and its mass was determined. A viscous liquid was obtained by drying an emulsion of gamboge at 110 C in the oven which underwent no further change in weight on storage in the oven. Other ways of determining density was by the determination of density of the glassy substance that obtained from a dried emulsion, which was identical to the material of the grains, or by energetic centrifugation of the emulsion after adding Potassium Bromide.

To determine the volume of the grains, Perrin did direct measurements of the radius of the grains by applying Stoke's law after determining the sedimentation velocity of the grains.He nearly managed to evaporate the fluid, leaving behind the grains which due to the capillary forces between them, formed rows and areas.Perrin minimized the error that would occur due to diffraction in a magnified image of the grain by measuring the length or surface area of a known number of grains in a row or area.

2.5.2 Determination of Avogadro's number

Perrin realised that the grains were being held in equilibrium against gravity due to the scattering effect of Brownian motion. It was shown that the decrease in number density with altitude is less for a gas of greater gram molecular weight. His insight that there may exist a possible analogy between the motion of gas molecules and the motion of the colloidal particles led to later developments in the kinetic theory of gases. The equation that he used to calculate the Avogadro number has the following form.

$$N_{AV} = -\frac{RT}{V(D-d)gH}\ln\left(\frac{n}{n_0}\right) \tag{2.25}$$

where n is the number density of grains at height H, n_0 is the number density of grains at height $H = 0$, D is the mass density of the grains and d is the mass density of the liquid, T is the absolute temperature and V is the volume of each grain. The rest of the symbols have their usual meanings.He calculated the grain density at various heights by placing a foil with a tiny hole in it in the focal plane. A shutter was placed in the path of the light rays that were illuminating the preparation and it was possible to estimate by eye the number of grains that were passing through a certain height at any point of time. 200 such readings were taken and averaged. The radius of the sphere of impact of each molecule was also calculated as was the mean free path. The Clausius and the Maxwell relations were used.

Another method used to determine the Avogadro number was the displacement in a given time. Using a camera lucida of known magnification, the positions occupied by grains at successive time intervals were determined. Perrin used the Einstein relation for the Diffusion constant to determine the Avogadro's number from this.

$$N_{AV} = \frac{t}{\langle x^2\rangle}\frac{RT}{3\pi a\eta} \tag{2.26}$$

where a is the radius of the grain and η is the viscosity of the fluid. Perrin showed that Stoke's law is also applicable for microscopic spheres and the equation above is applicable for the emulsions that he used to determine the root mean square velocity of the grains.

Other methods used by Perrin to determine the Avogadro's number included diffusion and rotational diffusion measurements. The rotational diffusion measurements were done with grains of the size of 50 μm with inclusions of water so that the rotational diffusion was visible.Diffusion measurements were done with grains larger in size placed in a vessel with an object glass on top into which the grains were absorbed.The diffusion constant was calculated from the increase in the number of grains absorbed into the object glass.

Chapter 3

A step further:Langevin equations and the Fokker Planck equation

The random motion of the Brownian particle is due to the collisional forces on the particle due to the particles of the fluid. This is, in effect a transfer of energy from the degrees of freedom of the heat bath at a temperature T and the degrees of freedom of the particle, until thermal equilibrium is established.At equilibrium the mean of the velocity squared goes as (T/m). In order to maintain the value of this average, the collisional forces bring the system into equilibrium.The time average of the collisional force exerted on a diffusing particle is the dissipative force $-\gamma v$. There is also a time dependent fluctuating force that acts on the particle, whose average is zero. Thus while reformulating the theory of Brownian motion, Langevin assumed the presence of

- A viscous force which is given by $-\gamma\frac{dx}{dt}$ where $\gamma = 6\pi\nu r$ where ν is the viscosity of the medium.
- A fluctuating force $\eta(t)$ which models the impact of the molecules of the liquid on the pollen grains. It is random in nature, both positive and negative and it maintains the agitation of the pollen which would otherwise be stopped due to the viscosity of the fluid medium.

This can then be written as a Newtonian equation of motion as,

$$\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} + \eta(t) \tag{3.1}$$

Multiplying by x and averaging, we get,

$$\frac{1}{2}\frac{d^2\langle x^2\rangle}{dt^2} + \frac{\gamma}{2}\frac{d\langle x^2\rangle}{dt} = K_BT \tag{3.2}$$

as the mean kinetic energy at equilibrium of the Brownian particles is $\langle\frac{1}{2}mv^2\rangle = \frac{1}{2}K_BT$, and as the fluctuating force is random in nature, $\langle\eta(t)\rangle$ is set to zero. Rather than considering a time average, an ensemble average is considered, such that an ensemble of possible random forces is chosen in such a manner that it is equivalent to the equilibrium ensemble and this averages the stochastic random force to zero. Assuming a Markovian system when the noise at different instants of time are uncorrelated we also have the relation $\langle\eta(t)\eta(t')\rangle = 2B\delta(t-t')$, where B is a constant.The probability distribution of the fluctuating force or the *noise* as it is generally referred to, can now be written as a Gaussian,

$$P[\eta(t)] = \frac{1}{\sqrt{4\pi B}}e^{-\frac{1}{4B}\int dt\eta^2(t)} \tag{3.3}$$

The power spectrum or the Fourier transform of the correlation function $\langle \eta(t)\eta(t') \rangle$ is thus given by,[26]

$$I(\omega) = C_{\eta\eta}(\omega) = 2B$$

that is, it is frequency independent. This type of noise is known as Markovian or white noise source. Equation (3.2) gives the solution,

$$\frac{d\langle x^2 \rangle}{dt} = \frac{2K_BT}{\gamma} + Ce^{-\gamma t} \tag{3.4}$$

As the decaying exponential reaches zero after a very small lapse of time, we have,

$$\langle x^2(t) \rangle - \langle x^2(0) \rangle = 2(K_BT\gamma)t \tag{3.5}$$

This is the Einstein's equation, identifying $D = K_BT\gamma$.
Langevin's assumption of $\langle \eta(t) \rangle$ vanishing is the same as Einstein's assumption that the value of the displacement δ is independent of the previous history of motion of the particle. It however adds an additional decaying exponential term which is later neglected, which did not appear in Einstein's derivation.

The Langevin's equation is a linear first order inhomogeneous equation. Using the condition that at thermal equilibrium we require $\langle v^2 \rangle_{eq} = KT/m$. The general solution of this equation is given by,[10]

$$v(t) = e^{-\gamma t}v(0) + \int_0^t dt' e^{-\gamma(t-t')}\eta(t') \tag{3.6}$$

The first term gives the exponential decay of the initial velocity. It is evident that in the absence of the fluctuating force $\eta(t)$ at long times the initial velocity would not reach its equilibrium value, but would instead decay to zero. In order to obtain the mean squared velocity we consider the contributions to $(v(t))^2$. They are as follows

- $e^{-2\gamma t}v(0)^2$ which obviously decays to zero at long times
- The two cross terms, $2v(0)e^{-\gamma t}\int_0^t dt' e^{-\gamma(t-t')}\eta(t')$ which vanish when averaged over the noise.
- The final term is second order in noise, $\int_0^t dt' e^{-\gamma(t-t')}\eta(t')\int_0^t dt" e^{-\gamma(t-t")}\eta(t")^2$. The two time noise correlation is, $2B\delta(t'-t")$.
  Thus after averaging we get $\int_0^t dt' e^{-\gamma(t-t')}\int_0^t dt" e^{-\gamma(t-t")}2B\delta(t'-t")^2$.

Performing the integrations we get,

$$\langle v(t)^2 \rangle = e^{-2\gamma t}v(0)^2 + \frac{B}{\gamma}(1 - e^{-2\gamma t}) \tag{3.7}$$

In the long time limit, the exponentials go to zero and the mean squared velocity approaches B/γ. In the long time limit however the mean square velocity must approach K_BT and hence we can identify,

$$B = \gamma K_BT \tag{3.8}$$

This is another form of the fluctuation dissipation theorem already mentioned in equation (2.12). It relates the strength B of the random noise to the magnitude of the dissipative force γ.

3.1 Correlation functions and the Diffusion coefficient

In non-equilibrium statistical mechanics, the absence of a "unique non-equilibrium state" in analogy with equilibrium statistical mechanics makes characterisation of the system using partition functions impossible. Instead time correlation functions indicate various important properties of the non-equilibrium system, such as,viscosity, thermal conductivity and diffusion.Time correlation functions are calculated by studying the long time of a certain time dependent quantity. We first time average the quantity, say, A itself and then calculate its fluctuation, $\delta A(t) = A(t) - \langle A \rangle$. Fluctuations at different times are often correlated. This correlation can be calculated as,

$$C(t) = \frac{1}{\tau} \int_0^\tau ds \delta A(s) \delta A(t+S) \tag{3.9}$$

3.1.1 Velocity velocity correlation

The system under consideration is ergodic and hence the long time average is equal to the ensemble average. Thus we average the expression for velocity over noise and then the initial velocity. The noise average leads to the expression,

$$\langle v(t) \rangle_{noise} = e^{(\tau)t} v(0) \tag{3.10}$$

Multiplying by $v(0)$ and averaging over the initial velocity, we get,

$$\langle v(t)v(0) \rangle_{eq} = K_B T e^{-(\gamma)t} \tag{3.11}$$

This holds in the positive time regime where Langevin's equation is valid. The long time (τ) average of the velocity correlation gives,

$$\langle v(t)v(t') \rangle_{time} = \frac{1}{\tau} \int_0^\tau ds v(t+s) v(t'+s) \tag{3.12}$$

Assuming that the initial condition was in the infinite past and that the contribution from the initial velocity has decayed to zero. The only contribution is from the noise and we obtain,

$$v(t) = \int_0^\infty e^{-(\gamma)u} \eta(t-u) du \tag{3.13}$$

The velocity correlation function thus becomes,

$$\begin{aligned} \langle v(t)v(t') \rangle_{time} &= \int_0^\infty du_1 \int_0^\infty du_2 e^{-(\tau)(u_1+u_2)} \frac{1}{\tau} \int_0^\tau ds \eta(t-u_1+s)\eta(t'-u_2+s) \\ &= \int_0^\infty du_1 \int_0^\infty du_2 e^{-(\tau)(u_1+u_2)} \frac{1}{\tau} \int_0^\tau ds 2B\delta(t-u_1-t'+u_2) \\ &= \frac{1}{2\gamma} e^{-\gamma|t-t'|} 2B \end{aligned} \tag{3.14}$$

On using the value of B from the fluctuation dissipation theorem that has already been found we, get,

$$\langle v(t)v(t') \rangle_{time} = K_B T e^{-\gamma|t-t'|} \tag{3.15}$$

Thus it is shown that the time and the ensemble averages give us the same result.

If we now consider the net displacement of the particle from time $t = 0$ to time $t = t$,

$$x(t) \int_0^t ds\, v(s) \tag{3.16}$$

The ensemble average of the mean squared displacement is,

$$\begin{aligned} \langle x^2 \rangle &= \langle \int_0^t ds_1 v(s_1) \int_0^t ds_2 v(s_2) \rangle \\ &= \int_0^t ds_1 \int_0^t ds_2 \langle v(t_1) v(t_2) \rangle \end{aligned} \tag{3.17}$$

Taking a time derivative we obtain,

$$\frac{\partial \langle x^2 \rangle}{\partial t} = 2 \int_0^t ds \langle v(t) v(s) \rangle \tag{3.18}$$

The equilibrium average is time translation invariant and hence we can write,

$$\frac{\partial \langle x^2 \rangle}{\partial t} = 2 \int_0^t ds \langle v(t-s) v(0) \rangle \tag{3.19}$$

The velocity correlation decays to zero in usually very short times. Only in long times can the diffusion equation be valid. In the long time limit the left hand side of the above equation tends to the diffusion coefficient $2D$ and thus we have the relation between a transport coefficient and a time correlation function,

$$D = \int_0^\infty dt \langle v(t) v(0) \rangle \tag{3.20}$$

3.1.2 Langevin equation from Hamiltonian: Harmonic Oscillator in a heat bath

The Langevin equation can also be derived from the Hamiltonian. This is a specific example of this method in which an arbitrary non-linear system is bilinearly coupled with a harmonic oscillator heat bath. We set up the Hamiltonian for this system and the external heat bath in the following manner.[10]

$$H_{system} = \frac{p^2}{2} + U(x) \tag{3.21}$$

$$H_B = \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \left(q_j - \frac{\gamma_j}{\omega_j^2} x^2 \right)^2 \right) \tag{3.22}$$

where H_{system} is the Hamiltonian of the system and H_B is the Hamiltonian of the Heat Bath under consideration.
The corresponding Hamilton's equations of motion for the system then give.

$$\begin{aligned} \frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -U'(x) + 2 \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x^2 \right) \end{aligned} \tag{3.23}$$

and for the bath,

$$\begin{aligned} \frac{dq_j}{dt} &= p_j \\ \frac{dp_j}{dt} &= -\omega_j^2 q_j + \gamma_j x \end{aligned} \tag{3.24}$$

These are the equations that describe a particle when it is connected to a heat bath. From the above equations, we get an inhomogeneous Harmonic Oscillator equation of motion for q_j as follows.

$$\frac{d^2q_j}{dt^2} = -\omega_j^2 q_j + \gamma_j x \tag{3.25}$$

The solution is,

$$q_j(t) = \cos\omega_j t\, q_j(0) + \frac{\sin\omega_j t}{\omega_j t} p_j(0) + \gamma_j \int_0^t ds\, x(s) \frac{\sin\omega_j(t-s)}{\omega_j} \tag{3.26}$$

We can integrate by parts to obtain,

$$q_j(t) - \frac{\gamma_j}{\omega_j^2}x(t) = \left(q_j(0) - \frac{\gamma_j}{\omega_j^2}x(0)\right) + p_j(0)\frac{sin\omega_j t}{\omega_j} - \gamma_j \int_0^t ds \frac{p(s)}{m}\frac{cos\omega_j(t-s)}{\omega_j^2} \tag{3.27}$$

When this is substituted in the equation for dp/dt in (3.23) we get the formal Langevin equation as,

$$\frac{dp}{dt} = -U'(x(t)) - \int_0^t ds\, K(s)p(t-s) + F_p(t) \tag{3.28}$$

The memory function $K(s, t-s)$ is

$$K(s, t-s) = \sum_j \frac{\gamma_j^2}{\omega_j^2} cos\omega_j t \tag{3.29}$$

and the noise $\eta(t)$ is given by,

$$\eta(t) = \sum_j \gamma_j p_j(0)\frac{sin\omega_j t}{\omega_j} + \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2}x(0)\right) cos\omega_j t \tag{3.30}$$

In order to compute fluctuation dissipation relations in this system we assume that the initial conditions are taken from a distribution

$$f_{eq}(p, q) \propto \exp(-H_B/K_B T)$$

in which the bath is in thermal equilibrium with respect to a frozen or constrained system co-ordinate $x(0)$. Then we have the following relations,

$$\begin{aligned} \left\langle q_j(0) - \frac{\gamma_j}{\omega_j^2} \right\rangle &= 0 \\ \left\langle p_j(0) - \frac{2\gamma_j}{\omega_j^2}p(0) \right\rangle &= 0 \\ \left\langle \left(q_j(0) - \frac{\gamma_j}{\omega_j^2}\right)^2 \right\rangle &= \frac{K_B T}{\omega_j^2} \end{aligned} \tag{3.31}$$

$$\left\langle \left(p_j(0) - \frac{2\gamma_j}{\omega_j^2}(p(0))^2\right)^2 \right\rangle = K_B T \tag{3.32}$$

Using these conditions in the expression for the noise $\eta(t)$, we get the fluctuation dissipation theorem,

$$\langle \eta(t)\eta(t') \rangle = K_B T\, K(t-t') \tag{3.33}$$

3.2 The Fokker Planck equation

As we have already seen, the Langevin equation can be used to determine time correlation functions which are integral to the calculation of important properties of the system. It can also be used to form the equation for the time evolution of the probability distributions, which is known as the Fokker Planck equation.

The Langevin equation of motion can be re written as

$$\frac{dp}{dt} = -\gamma p + \eta(t) = -\alpha \frac{\partial \mathcal{H}}{\partial p} + \eta(t) \tag{3.34}$$

where $\alpha = m\gamma$, $\langle \eta(t) \rangle = 0$ and $\langle \eta(t)\eta(t') \rangle = 2\alpha T \delta(t - t')$.
The probability that a diffusing particle has momentum p at a time t when it had a momentum p_0 at an earlier time t_0 is given by,

$$P(p, t|p_0, t_0) = \langle \delta(p - p(t)) \rangle_{p_0, t_0} \tag{3.35}$$

Thus the total probability that a particle has momentum p at time $t + \Delta t$ is,

$$P(p, t + \Delta t|p_0, t_0) = \int dp' P(p, t + \Delta t|p', t) P(p', t|p_0, t_0) \tag{3.36}$$

where the conditional probability $P(p, t + \Delta t|p', t) = \langle \delta(p - p(t + \Delta t)) \rangle_{p', t}$ can be calculated from the equation of motion of $p(t)$,

$$p(t + \Delta t) = p' - \alpha \frac{\partial \mathcal{H}}{\partial p'} \Delta t + \int_t^{t+\Delta t} dt' \eta(t') \tag{3.37}$$

The average of the noise goes to zero but the integral of its time correlation function is,

$$\int_t^{t+\Delta t} dt_1 \int_t^{t+\Delta t} dt_2 \langle \eta(t_1)\eta(t_2) \rangle = 2\alpha T \Delta t \tag{3.38}$$

Expanding the expression for the conditional probability $P(p, t + \Delta t|p', t)$ to first order, we get,

$$\langle \delta(p - p(t + \Delta t)) \rangle_{p', t} = \left[1 + \Delta t \alpha \frac{\partial \mathcal{H}}{\partial p'} \frac{\partial}{\partial p} + \Delta t \alpha T \frac{\partial^2}{\partial p^2} \right] \delta(p - p') \tag{3.39}$$

Using equation (3.35) we now can calculate the equation for the time evolution of the probability as,

$$\frac{\partial P}{\partial t} = \alpha T \frac{\partial}{\partial p} \left[\left(\frac{1}{T} \frac{\partial \mathcal{H}}{\partial p} + \frac{\partial}{\partial p} \right) P \right] \tag{3.40}$$

At steady state, when $\partial P / \partial t$ is zero we get back the Maxwell-Boltzmann distribution,

$$P_{eq} \sim e^{-\mathcal{H}(p)/T}$$

While this probability distribution has been derived in velocity space, in position space, we would have obtained a similar equation. However it would be known as the Smoluchowski equation.

The Fokker Planck equation can be derived more simply by considering that the probability of finding the particle at the phase space coordinate y at time $t+\Delta t$ is the probability of finding the particle at some coordinate $y-\xi$ at some earlier time t multiplied by the transition probability w of the particle going from all other possible coordinates separated by a displacement ξ from y.

$$P(y,t+\Delta t)=\int_{-\infty}^{+\infty}P(y-\xi,t)w(y-\xi|\xi)d\xi \tag{3.41}$$

Expanding till second order terms we have,

$$\int_{-\infty}^{+\infty}d\xi P(y,t)w(y|\xi)-\int_{-\infty}^{+\infty}d\xi\xi\frac{\partial}{\partial y}(P(y,t)w(y|\xi))+\frac{1}{2}\int_{-\infty}^{+\infty}\xi^2\frac{\partial^2}{\partial y^2}(P(y,t)w(y|\xi)) \tag{3.42}$$

We know that the transition probability obeys $\int_{-\infty}^{+\infty}d\xi w(y,\xi)=1$. Thus we get the Fokker Planck equation as,

$$\frac{\partial P}{\partial t}=\sum_i\frac{\partial}{\partial y_i}\left[\left(\lim_{\Delta t\to 0}\frac{\langle\xi_i\rangle}{\Delta t}\right)P(y_1...y_i...y_n,t)\right]+\frac{1}{2}\sum_{i,j}\frac{\partial}{\partial y_i\partial y_j}\left[\lim_{\Delta t\to 0}\frac{\langle\xi_i\xi_j\rangle}{\Delta t}P\right] \tag{3.43}$$

where a generalisation to multi-component y has been made. The Langevin equation provides the terms required and the Fokker Planck equation can describe the time evolution of the probability in x or v space. It can also describe probabilities in which exist, x and v coupling.

3.3 Methods of solution of the Fokker Planck equation

The FPE is a second order parabolic partial differential equation and in order to solve it, we need boundary conditions and initial conditions to confine y to an interval. The boundary conditions can be derived from general considerations in the following manner.Considering the FP equation of the form,

$$\partial_t p(\mathbf{z},t)=-\sum_i\frac{\partial}{\partial z_i}A_i(\mathbf{z},t)p(\mathbf{z},t)+\frac{1}{2}\sum_{i,j}\frac{\partial^2}{\partial z_i\partial z_j}B_{ij}(\mathbf{z},t)p(\mathbf{z},t) \tag{3.44}$$

This can be written in the form of a continuity equation.

$$\frac{\partial p(\mathbf{z},t)}{\partial t}+\sum_i\frac{\partial}{\partial z_i}\mathbf{J}(\mathbf{z},t)=0 \tag{3.45}$$

where $\mathbf{J}(\mathbf{z},t)=-A_i(\mathbf{z},t)p(\mathbf{z},t)+\frac{1}{2}\sum\limits_j\frac{\partial}{\partial z_j}B_{ij}(\mathbf{z},t)p(\mathbf{z},t)$.

The above equation can be written in an integral form. Considering a region R bounded by a surface S and defining,

$$P(R,t)=\int_R d\mathbf{z}p(\mathbf{z},t) \tag{3.46}$$

The equation (5.45) can be written as,

$$\frac{\partial P(R,t)}{\partial t}=-\int_s dS\mathbf{n}.\mathbf{J}(\mathbf{z},t) \tag{3.47}$$

This equation shows that the total loss of probability from region R is given by the surface integral of $\mathbf{J}$ over the surface bounding R, that is, S. We can thus calculate the net probability of crossing a surface S_{21} from region R_2 to region R_1 by subtracting the probability of crossing from region R_1 to region R_2 from the probability of crossing from region R_2 to region R_1. For

example, the latter is the joint probability of being at R_2 at time t and at R_1 at time $t + \Delta t$. This net probability divided by Δt gives,

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{R_1} d\mathbf{x} \int_{R_2} d\mathbf{y}[p(\mathbf{x}, t + \Delta t|\mathbf{y}, t) - p(\mathbf{y}, t + \Delta t|\mathbf{x}, t)]$$
$$= \int_{R_1} d\mathbf{x} \int_{R_2} d\mathbf{y}[\partial_{t'} p(\mathbf{x}, t'|\mathbf{y}, t) - \partial_{t'} p(\mathbf{y}, t'|\mathbf{x}, t)] \tag{3.48}$$

by considering that

$$\int_{R_1} d\mathbf{x} \int_{R_2} d\mathbf{y} p(\mathbf{x}, t|\mathbf{y}, t) = 0 \tag{3.49}$$

as this is the probability of being in R_1 and R_2 simultaneously. Using the Fokker Planck equation in the form (3.45) and applying the Divergence theorem, and using equation (3.46) we get for the net probability of crossing the surface S_{21},

$$\int_{s_{21}} dS\mathbf{n}.\{\mathbf{J}(\mathbf{x}, t|R_1, t) + \mathbf{J}(\mathbf{x}, t|R_2, t)\} \tag{3.50}$$

The integral over S_1 and S_2 have vanished as they involved the simultaneous probabilities of being in R_1 and R_2 at the same time. Only the integrals over S_{21} survives. Thus the coordinate $\mathbf{x}$ belongs to the union of R_1 and R_2, and we can write the net probability as,

$$\int_{S_{21}} dS\mathbf{n}.\mathbf{J}(\mathbf{x}, t) \tag{3.51}$$

where $\mathbf{n}$ points from R_2 to R_1.

There are several types of boundary conditions such as reflecting and absorbing boundaries, entrance and exit boundaries etc. However I shall only briefly discuss the cases of Periodic Boundaries and Boundaries at Infinity.

3.3.1 Periodic boundaries

The process is assumed to take place in an interval $[a, b]$ and the two end points are defined with respect to each other. An example of this case is diffusion on a circle. We can then impose the following boundary conditions,

$$\lim_{x \to b_-} p(x, t) = \lim_{x \to a_+} p(x, t) \tag{3.52}$$

$$\lim_{x \to b_-} J(x, t) = \lim_{x \to a_+} J(x, t) \tag{3.53}$$

The functions $A(x, t)$ and $B(x, t)$ in the FP equation are usually periodic in this interval so that,

$$\begin{aligned} A(a, t) &= A(b, t) \\ B(a, t) &= B(b, t) \end{aligned} \tag{3.54}$$

Equations (3.52) and (3.53) then reduce to equalities of $p(x, t)$ and its derivatives.

3.3.2 Boundaries at Infinity

Boundaries can occur at infinity provided that the probability $p(x,t)$ is well-behaved enough to be normalisable. This requires the following conditions,

$$\begin{aligned} \lim_{x\to\infty} p(x,t) &= 0 \\ \lim_{x\to\infty} \partial_x p(x,t) &= 0 \end{aligned} \tag{3.55}$$

When there are boundaries at $x = \pm\infty$ and nonzero currents at infinity are allowed, we have two possibilities,

$$\begin{aligned} (i)\ J(\pm\infty,t) &= 0 \\ (ii)\ J(+\infty,t) &= J(-\infty,t) \end{aligned} \tag{3.56}$$

3.3.3 Stationary solutions for homogeneous Fokker Planck equations

In a homogeneous process the drift and diffusion coefficients are time independent. The equation satisfied by the stationary solution is,

$$\frac{d}{dx}[A(x)p_s(x)] - \frac{1}{2}\frac{d^2}{dx^2}[B(x)p_s(x)] = 0 \tag{3.57}$$

This can be written in terms of the current as,

$$\frac{dJ}{dx} = 0 \tag{3.58}$$

which has the solution $J(x) = constant$. If the process takes place on an interval (a,b) then we have,

$$J(a) = J(x) = J(b) = J \tag{3.59}$$

If one of the boundaries are reflecting, it means both are reflecting, and we have $J = 0$.If the boundaries are not reflecting it means the boundary conditions to be used are periodic.

3.3.4 Zero current:Potential solution

We have the possibility of a zero current situation if the boundaries in an interval (a,b) are reflecting or if the boundaries are at infinity. Setting $J = 0$ we write,

$$A(x)p_s(x) = \frac{1}{2}\frac{d}{dx}[B(x)p_s(x)] = 0 \tag{3.60}$$

for which we have the solution of the form,

$$p_s(x) = \frac{\mathcal{N}}{B(x)} \exp[2\int_x^a dx' A(x')/B(x')] \tag{3.61}$$

where the normalisation constant $\mathcal{N}$ is determined from

$$\int_a^b p_s(x)dx = 1 \tag{3.62}$$

3.3.5 Periodic Boundary Conditions

In presence of a non zero current J we write the FP equation in the form,

$$A(x)p_s(x) - \frac{1}{2}\frac{d}{dx}[B(x)p_s(x)] = J \tag{3.63}$$

J is determined by the normalisation and the periodic boundary conditions,

$$\begin{aligned} p_s(a) &= p_s(b) \\ J(a) &= J(b) \end{aligned} \tag{3.64}$$

Defining

$$\psi(x) = \exp[2\int_x^a dx' A(x')/B(x')] \tag{3.65}$$

the solution of (3.63) becomes,

$$p_s(x)B(x)/\psi(x) = p_s(a)B(a)/\psi(a) - 2J\int_a^x \frac{dx'}{\psi(x')} \tag{3.66}$$

By using the Boundary conditions (3.64) we have the solution as,

$$J = \left[\frac{B(b)}{\psi(b)} - \frac{B(a)}{\psi(a)}\right]\frac{p_s(a)}{\int_a^b \frac{dx'}{\psi(x')}} \tag{3.67}$$

3.4 Diffusing particles in a gravitational field

An overdamped limit of the Brownian particle moving in a constant external gravitational field is considered. The overdamped limit means that the acceleration term in the Langevin equation drops out and we have for unit mass particles,

$$dx = -\frac{g}{\gamma}dt + \frac{\sqrt{2D}}{\gamma}\eta(t)dt \tag{3.68}$$

The Fokker Planck equation for this case becomes,

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left(\frac{g}{\gamma}\right) + \frac{1}{2}\frac{2D}{\gamma^2}\frac{\partial^2 p}{\partial x^2} \tag{3.69}$$

Taking $\gamma = 1$ we have the steady state solution to this equation as,

$$p_s(x) = \mathcal{N}\exp[-gx/D] \tag{3.70}$$

Considering this solution on an interval (a, b) we find that if a is finite and b is infinite, the solution is normalisable. This only shows that particle diffusing in a container will fall, and if the beaker is infinitely deep, they will continue to fall. The case of particles diffusing upwards against gravity, has a decaying exponential term in the probability as can be seen and almost never occurs.

If the boundary conditions are periodic the particles pass from the boundaries and back, and implementation of the periodic boundary conditions yields a constant probability.

Chapter 4

Thermodynamics: A brief review

The laws of thermodynamics are found to be in excellent agreement with observation. However these deal with macroscopic systems with large number of components or degrees of freedom.[25]

4.0.1 Energy Conservation and the First Law of Thermodynamics

Let ΔQ denote the total amount of heat absorbed by the system and ΔW be the work done by the system. Thus we can define the change in a quantity (a state function) known as the internal energy of the system, as,[1]

$$\Delta U = \Delta Q - \Delta W \tag{4.1}$$

The internal energy state function is the total energy associated with the internal degrees of freedom of the system. The experimental foundation of the above equation lies in the demonstration of the equivalence of heat and mechanical energy, as demonstrated by Joule. The recognition of heat as a form of mechanical energy enables the casting of the First law as a law of conservation of energy. For infinitesimal transformations, we can write the above equation as,

$$\delta Q = dU + \delta W \tag{4.2}$$

4.0.2 Second law of Thermodynamics

The Kelvin Statement: There exists no thermodynamics transformation whose sole effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work. *The Clausius Statement*: There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir. The Second Law of thermodynamics allows us to define a state function known as entropy. This is possible due to the **Clausius theorem**. The Clausius Theorem has the following statement.

In any cyclic transformation in which the temperature is defined, the following inequality holds,

$$\int_{\mathcal{C}} \frac{dQ}{T} \leq 0 \tag{4.3}$$

where the integral extends over one cycle of the transformation. The equality holds if the cyclic transformation is reversible.

The proof of this is, as follows,
Let us consider a cyclic transformation $\mathcal{C}$ which can be divided into n infinitesimal steps, such that the temperature remains constant in each step. This can also be considered to be the system in contact with n heat reservoirs with temperatures T_i where $i = 1, n$. Let Q_i be the amount of heat absorbed by the system during the ith step from the heat reservoir at the temperature T_i. n Carnot engines are then constructed such that the ith Carnot engine C_i

- operates between T_i and T_0 ($T_0 \geq T_i$,for all i)
- absorbs Q_i^0 amount of heat from reservoir at T_0
- rejects Q_i amount of heat to reservoir at T_i

From the definition of the temperature scale in the context of Carnot engines,

$$\frac{Q_i^0}{Q_i} = \frac{T_0}{T_i}$$

Considering one cycle of the combined operation $\mathcal{C} + \Sigma_i C_i$. The net result is that an amount of heat

$$Q_0 = \Sigma_{i=1}^n Q_i^0 = T_0 \Sigma_{i=1}^n \left(\frac{Q_i}{T_i}\right)$$

is absorbed from the reservoir T_0 and converted entirely into work, without any other effect. According to the second law this is impossible unless $Q_0 \leq 0$. Therefore,

$$\Sigma_{i=1}^n \left(\frac{Q_i}{T_i}\right) \leq 0$$

If $\mathcal{C}$ is reversible, on reversing the cycle, we find that the Q_is now have a negative sign. Thus we have,

$$-\Sigma_{i=1}^n \left(\frac{Q_i}{T_i}\right) \leq 0$$

This combined with the previous inequality, which still holds for a reversible cycle $\mathcal{C}$ gives.

$$\int_{\mathcal{C}} \frac{dQ}{T} = 0 \tag{4.4}$$

Now let us define the initial and final states as A and B.Let I and II be two arbitrary reversible paths joining A and B. Let II' be the reverse of path II. According to Clausius' Theorem,

$$\int_I \frac{dQ}{T} + \int_{II'} \frac{dQ}{T} = 0$$

But,

$$\int_{II'} \frac{dQ}{T} = -\int_{II} \frac{dQ}{T}$$

Therefore,

$$\int_I \frac{dQ}{T} = \int_{II} \frac{dQ}{T}$$

Thus we may now define a state function known as the entropy which is defined by choosing an arbitrary initial point O. The entropy at some other point A is defined as,

$$S(A) = \int_O^A \frac{dQ}{T} \tag{4.5}$$

over any reversible path joining O and A. The entropy is defined only with an additive constant. The difference in entropy of two states is however defined as,

$$S(A) - S(B) = \int_A^B \frac{dQ}{T}$$

For any arbitrary transformation the change in entropy between the initial and the final states are given by,

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A) \tag{4.6}$$

such that the equality holds in the case of a reversible process. If we now consider a cyclic process such that states A and B are connected by a reversible path R and an irreversible arbitrary path X. From the Clausius theorem we have,

$$\int_X \frac{dQ}{T} - \int_R \frac{dQ}{T} \leq 0$$

As $\int_R \frac{dQ}{T} = \Delta S$,we get,

$$\Delta S - \int_X \frac{dQ}{T} \geq 0 \tag{4.7}$$

For an isolated system $\Delta S \geq 0$ by the Second Law. If we consider (system + reservoir) to be an isolated system, we have

$$\Delta S_{system} + \Delta S_{reservoir} \geq 0$$

We have defined the reservoir entropy as,

$$\Delta S_{reservoir} = -\int_x \frac{dQ}{T} \tag{4.8}$$

Chapter 5

Fluctuating Thermodynamics

The laws of thermodynamics are very well established as deviations from them are almost never observed, within the limits of experimental accuracy. However, this is because,the systems under consideration are usually very large and hence have a large number of degrees of freedom involved in them, of the order of 10^{23}. This condition is no longer true in the case of microscopic systems such as nano machines. An example of this might be the motor protein $\phi 29$ which crams the DNA into the empty shell of a virus, as it consumes energy and generates torque. Other than this the growing interest in nano scale machinery and more and more sophisticated experimental tools have heightened the need for better understanding of the laws that govern such microscopic systems. It is thus interesting to test the validity and find the deviations from the first and second law of thermodynamics for these kind of systems.

It is possible to derive the laws of thermodynamics starting from purely microscopic considerations [2],[3]. It has been shown that a class of relations known as the entropy production fluctuation relations are valid for systems that are arbitrarily far from equilibrium. These relate the ratio of the probability of the forward to the probability of the reverse process, to the entropy production of the system measured over a given time interval. Thus it is possible to arrive at an expression for entropy if the probabilities of the forward and reversed processes can be calculated.

In this project, we wish to consider the laws of thermodynamics as applicable to self propelled systems. Other than being a microscopic system which in itself is interesting, the self propelled system is a very special type of non equilibrium system. It has the ability by some chemical or other means to convert internal energy into mechanical energy with some dissipation. Thus we consider an active particle whose self propulsion property can be modelled by means of the action of a velocity dependant potential. We then consider this active particle, but now in a trap generated by a conservative potential. These dynamics can effectively be described by an appropriate Langevin equation. The transition probabilities are chosen to be a Gaussian function of the noise that arises due to the coupling of the system with the reservoir at the initial state, as the fluctuation brings about the relevant probabilistic nature of the process. We calculate the forward and reverse process probabilities to arrive at a definition of entropy.

The general formalism that we shall be using to test the validity of the first law of thermodynamics and to investigate the definition of entropy in the active Brownian particle case is as follows.
Let us consider the Langevin Equation of a particle in a conservative potential and under the action of an external force that obeys time reversal symmetry.

$$\ddot{x} = -\gamma\dot{x} + \eta - \partial_x V + f_{ext} \tag{5.1}$$

where V is the conservative potential. We can write the corresponding energy conservation equation by multiplying the Langevin equation by $\dot{x}$. This turns out to be in the form,

$$d\left(\frac{1}{2}\dot{x}^2 + V\right) = (-\gamma\dot{x} + \eta)dx + f_{ext}dx \tag{5.2}$$

The term $\int(-\gamma\dot{x} + \eta)dx$ represents the total heat supplied to the system. $\left(\frac{1}{2}\dot{x}^2 + V\right)$ is the change in internal energy of the system and $\int f_{ext}dx$ is the work done by the external force on the system.

Thus equation (2) takes the form of the first law of thermodynamics.

$$dE = \delta Q + \delta W$$

where δ denotes the imperfect differential.

The second law can be arrived at through the consideration that the probability of the forward and reverse process would depend upon the fluctuation η. This is because the other quantities in the Langevin equation are deterministic and depend only on the initial conditions. The only statistics that are being contributed are due to the fluctuation η. The process under consideration is assumed to be Markovian and thus the fluctuation is taken to be,

$$\langle\eta(t)\rangle = 0 \qquad \langle\eta(t)\eta(0)\rangle = 2D_0\delta(t) \tag{5.3}$$

If the time window is discretised then $\delta(t) \to \delta t$. Not considering higher moments the transition probability of the time evolution of the system along a path defined by $X = [x(t), v(t), f(t)]$ takes the form,

$$\mathcal{P}[\eta] = \mathcal{N}\delta(\dot{x} - v)e^{-(\eta^2/4D_0)\delta t} \tag{5.4}$$

Replacing the value of η^2 from the corresponding Langevin equation, We find the ratio of the transition probability of the forward process to that of the reversed process to be,

$$\frac{\mathcal{P}_F(2|1)}{\mathcal{P}_R(1|2)} = \exp\left[\frac{1}{D_0}\int_0^\tau dt\left(m\dot{v} + \frac{\partial U}{\partial x} - f(t)\right)g(v)\right] \tag{5.5}$$

Replacing the above expression from the Langevin Equation, we get,

$$\frac{\mathcal{P}_F(2|1)}{\mathcal{P}_R(1|2)} = e^{-\beta\int_1^2 dx(-\gamma\dot{x}+\eta)} \tag{5.6}$$

We have already defined $\int(-\gamma\dot{x} + \eta)dx$ as the heat supplied to the system. Thus we get,

$$\frac{\mathcal{P}_F(2|1)}{\mathcal{P}_R(1|2)} = e^{-\beta\Delta Q} \tag{5.7}$$

Now to compute the ratio between the total probability of the forward process to the total probability of the reverse process, we consider Π_i where $i = 1, 2$ is the initial and final equilibrium probability distributions.

$$\begin{aligned}\frac{P_F}{P_R} &= \frac{\Pi_1\mathcal{P}_F(2|1)}{\Pi_2\mathcal{P}_F(1|2)} \\ &= e^{\Delta s/K_B}\frac{\mathcal{P}_F}{\mathcal{P}_R}\end{aligned}$$

This is obtained from the consideration that the fluctuating entropy content of the initial and the final equilibrium states are given by $s = -K_B\ln\Pi$ such that $\frac{\Pi_1}{\pi_2} = \exp\Delta s/K_B$. By Jarzynski

and Crooks, [11] and [12] the equilibrium distributions are of the form,$\Pi_i = e^{-\beta(E_i - F_i)}$ where E and F are the internal energies and the Helmholtz free energies.
Therefore,the ratio of the probability distributions of the forward and the reverse processes is given by,

$$\frac{P_F}{P_R} = e^{\beta(\Delta E - \Delta F - \Delta Q)}$$

which can finally be expressed as,

$$\frac{P_F}{P_R} = e^{\beta(\Delta W - \Delta F)} = e^{\beta \Delta S_{total}} \tag{5.8}$$

This is equivalent to the expression,

$$\langle e^{-\Delta S_{total}/K_B T} \rangle = \int \mathcal{D}[X_f] \frac{P_R}{P_F} P_F \tag{5.9}$$

$$= \int \mathcal{D}[X_r] P_R[X_r] = 1 \tag{5.10}$$

where X_r and X_f respectively denote the paths taken by the system during the forward and the reversed processes.
Using the Jensen inequality, we obtain,

$$\langle \Delta S_{total} \rangle \geq 0 \tag{5.11}$$

which is the Second Law of thermodynamics defined for microscopic systems. From this we get the Jarzynski equality, that,

$$\langle e^{-\beta \Delta W} \rangle = e^{-\beta \Delta F} \tag{5.12}$$

Chapter 6

Fluctuating thermodynamics for self propelled particles

6.1 First law and energy conservation

The phenomenon of self propulsion can be modelled to certain levels of accuracy as a Brownian particle under the influence of a force derived from a velocity dependent potential. As is evident, for any velocity dependent force, it does not obey time reversal symmetry. We consider such a potential $\Phi(v)$ and write down the corresponding Langevin equation for the dynamics of the particle in the presence of a constant external force as,

$$\dot{v} = -\gamma v + F(v) - \frac{\partial U}{\partial x} + f(t) + \eta(t) \tag{6.1}$$

Multiplying the above equation by v we get,

$$\frac{d}{dt}(\frac{1}{2}mv^2) = -\gamma v^2 + F(v)v - v\frac{\partial U}{\partial x} + vf(t) + v\eta(t)$$

Integrating over time, we get,

$$\Delta\left(\frac{1}{2}mv^2 + U(x)\right) = \int dt\, v(-\gamma v + \eta(t)) + \int dt\, vf(t) + \int dt\, vF(v) \tag{6.2}$$

Although on averaging the Langevin equation and proceeding with this calculation, it would seem that there would only exist the dissipative term $-\gamma v^2$ and energy conservation would not hold.However from the above equation it is seemed, that even on taking a mean, in addition to the dissipative term, there is a contribution from $\langle x(t)\eta(t)\rangle$. For simplicity, considering the Langevin equation in the overdamped limit,we find that an $\langle \eta(t)\eta(t)\rangle$ correlation, which we already know is not zero.

Thus we note that the energy flow from the heat bath is given by $\delta Q = \int dtv(-\gamma v + \eta(t))$, the amount of energy transferred from the internal motor degrees of freedom to mechanical motion is given by $\delta Q_m = \int dtvF(v)$, the work done on the particle by $\Delta W = \int dtvf(t)$ and the change in energy of the internal degrees of freedom of the system as $\Delta E = \left(\frac{1}{2}mv^2 + U(x)\right)$. Thus the first law can be written as,

$$\Delta E = \delta Q + \Delta W + \delta Q_m \tag{6.3}$$

We also notice that in the absence of self propulsion, that is in the absence of the force $F(v)$ we regain the form of the first law for conventional Brownian particles,

$$\Delta E = \delta Q + \Delta W$$

6.2 Second law and the definition of entropy

Following the formalism outlined in the previous sub section,we find the probability of the forward process,

$$\mathcal{P}_F = \mathcal{N} \exp\left[-\frac{1}{4D_0}\int_0^\tau dt\left(m\dot{v} - g(v) + \frac{\partial U}{\partial x} - f(t)\right)^2\right] \tag{6.4}$$

where the velocity dependent terms are represented by $g(v)$, and the reverse process,

$$\mathcal{P}_R = \mathcal{N} \exp\left[-\frac{1}{4D_0}\int_0^\tau dt\left(m\dot{v} + g(v) + \frac{\partial U}{\partial x} - f(t)\right)^2\right] \tag{6.5}$$

Here it is assumed that all the velocity dependent terms are time reversal asymmetric.

Thus we find for the ratio of the transition probabilities of the forward and the reversed processes,

$$\frac{\mathcal{P}_F(2|1)}{\mathcal{P}_R(1|2)} = \exp\left[-\beta\int_0^\tau dt\left(m\dot{v} + \frac{\partial U}{\partial x} - f(t)\right)g(v)\right]$$

where $g(v) = -\gamma v + F(v)$ and $f(t) = f_{const} + f_t$ in this case.
This can be written as,

$$\frac{\mathcal{P}_F(2|1)}{\mathcal{P}_R(1|2)} = e^{-\beta(\Delta Q + \Delta Q_m + \Delta Q_{em} + (m/\gamma)\Delta\Phi)} \tag{6.6}$$

as $\gamma/D_0 = 1/K_BT = \beta$ and where $\Delta Q = \int_0^\tau dtv(-\gamma v + \eta)$ which is the heat absorbed by the system, $\Delta Q_{em} = \frac{1}{\gamma}\int_0^\tau dtF(v)(f(t) - \partial_x U)$ which, though it has no correspondence in the conventional theory of Brownian Motion, represents the coupling between the internal motor degrees of freedom and the external mechanical forces. The final term is the heat given by the internal degrees of freedom of the system and we denote this by ΔQ_m In order to find the ratio of the total probability of the forward and the reversed processes we must again find the initial probability distribution.
In the absence of any periodic boundary condition, the initial steady state is actually the zero current state and it is obtained from the Fokker Planck equation, Although it is a zero current state it cannot be equilibrium, but can called an equilibrium-like, non-equilibrium steady state (NESS),

$$\partial_t P = \partial_v\left[\left(\frac{\partial\tilde{\Phi}}{\partial v}\right)P + D_0\frac{\partial P}{\partial v}\right] \tag{6.7}$$

where $D_0 = \gamma K_BT$ The equilibrium-like distribution becomes,

$$P_{steady} = \mathcal{A}e^{-\tilde{\Phi}(v)/D_0} = \mathcal{A}e^{-\beta\frac{1}{2}mv^2}e^{-\beta\frac{m}{\gamma}\Phi(v)}e^{\beta\frac{m}{\gamma}f_{const}v} \tag{6.8}$$

where $\tilde{\Phi}(v) = \frac{1}{2}\gamma v^2 - \phi(v)$. Substituting we have for the ratio of the total probabilities,

$$\frac{P_F}{P_R} = e^{-\beta\frac{m\Phi(v)}{\gamma}|_2^1}e^{-\beta\frac{mv^2}{2}|_2^1}e^{\beta\frac{m}{\gamma}f_{const}\Delta v}\frac{\mathcal{P}_F}{\mathcal{P}_R} \tag{6.9}$$

According to equation (9) if we consider this essentially non-equilibrium system to be equilibrium-like, we have for the definition of the non equilibrium entropy,

$$\Delta S_{total} = \Delta s - \frac{1}{T}(\Delta Q + \Delta Q_m + \Delta Q_{em} + (m/\gamma)\Delta\Phi) \tag{6.10}$$

where Δs represents the change in the fluctuating entropy content between the initial and the final states. In the absence of the self propelling force $F(v)$ we find that the entropy becomes,

$$\Delta S_{total} = \Delta s - \frac{1}{T}\Delta Q \tag{6.11}$$

This is the same as equation (3.10), which is the definition of entropy we expect for a conventional Brownian particle.

$$\langle e^{-\Delta S_{total}/K_B T}\rangle = \int \mathcal{D}[X_f]\frac{P_R}{P_F}P_F \tag{6.12}$$

$$= \int \mathcal{D}[X_r]P_R[X_r] = 1 \tag{6.13}$$

where X_r and X_f respectively denote the paths taken by the system during the forward and the reversed processes.
Using the Jensen inequality, we obtain,

$$\langle \Delta S_{total}\rangle \geq 0 \tag{6.14}$$

which is the Second Law of thermodynamics defined for self propelled microscopic systems. Thus the quantity that is to be maximized is the one denoted by ΔS_{total}.

Chapter 7

Linear response at steady state and modified fluctuation dissipation relations

Linear response theory deals with studying how a system responds to an external perturbation. The equilibrium linear response is concerned with characterising the response of a system at equilibrium to an external perturbation.In the simplest classical case, we can derive the equilibrium linear response from the Hamiltonian in the following manner.

The unperturbed system can be defined by the Hamiltonian $H(x)$, with the applied perturbing field being given by E such that the coupling of the external field to the degrees of freedom of the system can be represented in terms of an energy $-M(x)E$ where $M(x)$ is some known state function of the system. The perturbed Hamiltonian then becomes $H(x, E) = H(x) - M(x)E$. The static linear response is calculated by writing out the perturbed ensemble average of an arbitrary quantity of the system.

$$f(x, E) = \frac{1}{\mathcal{Z}(E)} \exp\left[-\beta(H(x) - M(x)E)\right] \tag{7.1}$$

where the partition function $\mathcal{Z}(E) = \int dx \exp\left[-\beta(H(x) - M(x)E)\right]$. Retaining only first order terms, we get the equilibrium ensemble average of f as

$$f(x, E) = [1 + \beta\{M(x) - \langle M\rangle\}E]f(x) \tag{7.2}$$

where $\langle M\rangle$ denoted the unperturbed equilibrium average. Considering a situation in which this is zero, we have for the static linear response of any dynamical variable A,

$$\langle A; E\rangle = \langle A\rangle + \chi_{AM}E \tag{7.3}$$

such that $\chi_{AM} = \beta\langle AM\rangle$. This can easily be extended to finding the time dependent response functions of a dynamical variable.

7.1 Fluctuation dissipation Theorems

The concepts of linear response theory can also be used to derive the fluctuation dissipation theorem (FDT) . As has already been discussed, it predicts how the response function of a thermodynamic observable is related to correlation of thermal fluctuations at equilibrium. Let us assume that an equilibrium system described by a Hamiltonian H is perturbed at time $t = t_1$ by an external force $h(t)$. The FDT predicts a response at a later time $t_2 > t_1$ [13]

$$R_A^{eq}(t_2 - t_1) = \frac{\delta\langle A(t_2)\rangle}{\delta h(t_1)} = \beta\frac{\partial}{\partial t_1}\langle A(t_2)[-\partial_h H(t_1)]_{h=0}\rangle_{eq} \tag{7.4}$$

where the correlation is calculated at equilibrium corresponding to temperature T with $\beta = 1/T$. The differential operator ∂_h in the above relation denotes the scalar derivative evaluated at time t_1. The Boltzman constant is assumed to be $K_B = 1$, unless otherwise stated. Using the Onsager regression hypothesis the FDT can be interpreted as follows – the decay of a fluctuation is independent of how it has been created,whether under the influence of a small applied force or spontaneously by thermal noise. Calculating the response of an appropriate quantity can also lead to a definition of temperature in the equilibrium case.In the non-equilibrium regime, modifications to the FDT can be expected. Attempts to define an effective temperature have been made **cite**. Such a definition is not possible in the case of self-propelled particles as shall be discussed later.The non-equilibrium violation of the FDT has been studied in context of glassy systems, granular matter,sheared fluid, stochastic processes, and biological systems [14, 15, 16, 13, 17, 18, 19, 20, 21].

In 1972 [28], G. S. Agarwal obtained a modified fluctuation-dissipation relation (MFDR) that related response functions around non-equilibrium steady states (NESS) to correlations evaluated at steady state. For a system evolving with statistical dynamics described by the Fokker-Planck (FP) equation $\partial_t p = \mathcal{L}_0 p$, Agarwal showed that a perturbation in the operator $\mathcal{L}_0 \to \mathcal{L}_0 + h(t)\mathcal{L}_1$ leads to a response that can be expressed in terms of a correlation function evaluated at the unperturbed steady state [28, 27],

$$R_A(t_2 - t_1) = \frac{\delta\langle A(t_2)\rangle}{\delta h(t_1)} = \langle A(t_2)M(t_1)\rangle \tag{7.5}$$

where the *Agarwal term* $M = [\mathcal{L}_1 p_s]/p_s$ with p_s denoting the steady-state probability distribution.

7.2 The Agarwal form of MFDR

The probability distribution $p(\varsigma, t)$ of finding a system at state ς at time t evolves with time as

$$\partial_t p(\varsigma, t) = \mathcal{L}(\varsigma, h)p(\varsigma, t) \tag{7.6}$$

where $\mathcal{L}$ is a general time evolution operator that depends on external force $h(t)$. For weak h, Taylor expanding the operator we get

$$\mathcal{L}(\varsigma, h) = \mathcal{L}_0(\varsigma) + h(t)\mathcal{L}_1(\varsigma) \tag{7.7}$$

where $\mathcal{L}_1 = [\partial_h \mathcal{L}]_{h=0}$. The solution to Eq. 7.6 is

$$p(\varsigma, t) = p_s + \int_{-\infty}^{t} d\tau e^{\mathcal{L}_0(t-\tau)} h(\tau)\mathcal{L}_1 p_s(\varsigma) \tag{7.8}$$

where p_s denotes the steady-state distribution that obeys $\mathcal{L}_0 p_s = 0$. Then the response of any observable $\langle A(t)\rangle = \int d\varsigma A(\varsigma)p(\varsigma, t)$ to a force $h(t)$ is

$$\begin{aligned} R_A(t_2 - t_1) &= \frac{\delta\langle A(t_2)\rangle}{\delta h(t_1)} = \int d\varsigma A(\varsigma)\frac{\delta p(\varsigma, t_2)}{\delta h(t_1)} \\ &= \int d\varsigma A(\varsigma) e^{\mathcal{L}_0(t_2-t_1)}\mathcal{L}_1 p_s(\varsigma) \\ &= \int d\varsigma A(\varsigma) e^{\mathcal{L}_0(t_2-t_1)} M(\varsigma) p_s(\varsigma) \end{aligned} \tag{7.9}$$

where in the last step we used the Agarwal term $M(\varsigma) \equiv [\mathcal{L}_1 p_s]/p_s$. By definition, the two-time correlation function is $\langle A(t)B(0)\rangle = \int d\varsigma \int d\varsigma' A(\varsigma)B(\varsigma')p_2(\varsigma, t; \varsigma', 0)$, where $p_2(\varsigma, t; \varsigma', 0)$ is the

joint probability distribution of finding the system at state ς' at time 0 and at state ς at time t. One can express $p_2(\varsigma, t; \varsigma', 0) = w(\varsigma, t|\varsigma', 0)\, p(\varsigma', 0)$ where $w(\varsigma, t|\varsigma', 0)$ is the transition probability. The time evolution $\partial_t p = \mathcal{L}_0 p$ can be solved to obtain the transition probability at steady state $w(\varsigma, t|\varsigma', 0) = \exp(\mathcal{L}_0 t)\delta(\varsigma - \varsigma')$. Thus the two-time correlation at steady state takes the form $\langle A(t)B(0)\rangle = \int d\varsigma A(\varsigma) \exp(\mathcal{L}_0 t) B(\varsigma) p_s(\varsigma)$. Therefore we can write Eq. 7.9 as

$$R_A(t_2 - t_1) = \langle A(t_2) M(t_1)\rangle. \tag{7.10}$$

This is the *Agarwal form* of MFDR [28]. The derivation presented here used a continuum notation of the phase space variable ς. However, the result is general, and can be derived similarly for a system that evolves through transitions between discrete states (see Eq. **??**).

The Agarwal term in its operator form $M(\varsigma) \equiv [\mathcal{L}_1 p_s]/p_s$ requires detailed knowledge of the probability distribution at steady state.

For the Fokker Planck equation that we are using we can identify $\mathcal{L}_0$ and $\mathcal{L}_1$ as follows

$$\mathcal{L}_0 = -\frac{d^2\phi}{dv^2} + \left(D_0 - \frac{d\phi}{dv}\right)\frac{d}{dv} \tag{7.11}$$

and

$$\mathcal{L}_1 = \frac{\partial}{\partial v} \tag{7.12}$$

For the case of Active Brownian systems we can write the Agarwal term as,

$$M(v) = \frac{\mathcal{L}_1 p_s}{p_s} = \frac{1}{D_0}\frac{\partial \tilde{\Phi}(v)}{\partial v} = -g(v)/D_0 = (\gamma v - F(v))/D_0 \tag{7.13}$$

$$\begin{aligned} \frac{\delta A(t_2)}{\delta h(t_1)} &= \frac{1}{D_0}\langle A(t_2)[\gamma v(t_1) - F(v(t_1))]\rangle \\ &= \beta\langle A(t_2)\ v(t_1)\rangle - \frac{1}{D_0}\langle A(t_2)\ F(v(t_1))\rangle \end{aligned} \tag{7.14}$$

Thus for any general velocity dependent potential, we can write the velocity response in the following form.

$$R_v(t) = -\frac{1}{K_B T}\int_0^\infty dt\langle v(t)v(0)\rangle + \frac{1}{D_0}\int_0^\infty dt \left\langle v(t)\ \frac{\partial \Phi}{\partial v}\right\rangle$$

This is actually the modified fluctuation dissipation relation for the mobility and can be written in the more familiar form as,

$$\mu = \frac{1}{K_B T}\int_0^\infty dt\langle v(t)v(0)\rangle - \frac{1}{D_0}\int_0^\infty dt\, \langle F(v)\ v(0)\rangle \tag{7.15}$$

Thus we see that the equilibrium FDT no longer holds in this scenario. The modification is caused due to the presence of the self propelling force $F(v)$ and in the absence of this force we regain the expected FDT for a Brownian particle. In the case of an equilibrium system, $\int_0^\infty dt\langle v(t)v(0)\rangle$ is just the equilibrium diffusion coefficient D. Thus the equilibrium FDT looks like,

$$\mu = \frac{1}{K_B T} D \tag{7.16}$$

Thus this FDT can be used to obtain the temperature of the system.

While there have been attempts to define an effective temperature for non-equilibrium systems [23], by defining an effective diffusion coefficient , this was only possible if the corrections to the equilibrium temperature or diffusion coefficient were multiplicative. As can clearly be seen from equation (7.15) the corrections that are obtained are additive, ruling out the possibility of defining an effective temperature for the non-equilibrium self propelled system.

Chapter 8

Models and Results

We now consider three models of self propulsion and using our formalism, calculate the entropy,and the response functions within their framework.

8.1 The Rayleigh Helmholtz model

One of the most commonly used models of self propulsion, this considers particles under the action of the potential $\Phi(v)$ of the form $-\frac{a}{2}v^2 + \frac{b}{4}v^4$, and $F(v) = \Phi'(v)$. In the deterministic limit, that is in the absence of fluctuations due to the presence of the heat bath etc, has two fixed points at $+_-\sqrt{a/b}$. If $a > \gamma$, this model generates an effective negative friction $\gamma' = \gamma - a$ and energy is pumped into the SPP. This model has been used to study Brownian motion of SPPs as well as to describe the bimodal velocity distribution of microtubules under the collective influence of a set of bidirectional motor proteins NK11.

8.1.1 Fluctuating thermodynamics for free particles

Assuming the presence of an external constant force f we can write the total force as $-\tilde{\Phi}'(v) = -\gamma v + F(v) + f$. This can be assumed to be derived from the velocity dependent potential, $\tilde{\Phi}(v) = (\gamma/2)v^2 + \Phi(v) - fv$ The Langevin equation for the velocity is in this case,

$$\dot{v} = -\tilde{\Phi}'(v) + \eta(t) \tag{8.1}$$

The first law can be obtained as elaborated in Chapter 5, this time in the case of a free self propelled particle, as

$$\Delta\left(\frac{1}{2}mv^2\right) = \int dt(-\gamma v + \eta(t)) + \int dtvf + \int dtv(av - bv^3) \tag{8.2}$$

Using the results of the previous chapters, we can define the following quantities.
The steady state distribution in this case is

$$p_s(v) = \mathcal{A}e^{-\beta\left(\frac{\tilde{\Phi}(v)}{\gamma}\right)}$$

The various contributions to the entropy in equation (5.8) become

$$\Delta Q_{em} = \frac{f}{\gamma}\int dt(av - bv^3) \tag{8.3}$$

$$\Delta Q_m = \int dt\, v(av - bv^3) \tag{8.4}$$

$$\Delta Q = \int dt(-\gamma v + \eta(t)) \tag{8.5}$$

The modified fluctuation dissipation relation can be written as,

$$\mu = \frac{1}{K_B T}\int_0^\infty dt\langle v(t)v(0)\rangle - \frac{1}{D_0}\int_0^\infty dt\left\langle (av - bv^3)\ v(0)\right\rangle \tag{8.6}$$

8.1.2 Self propelled particles in an external harmonic trap

We can extend this further to include an active self propelled particle in a harmonic trap.[22] The Langevin equation for this would read as,

$$m\dot{v} = \left(-\gamma - \frac{1}{v}\frac{\partial \Phi}{\partial v}\right)v + \omega_0^2 x + \sqrt{2D_0}\eta(t) \tag{8.7}$$

By multiplying the above equation with $\dot{v}$ we get a Langevin equation for the time evolution of the Hamiltonian.

$$\frac{dH}{dt} = -\gamma_H(H)H + \sqrt{2D_H H}\eta_H(t) \tag{8.8}$$

This equation is subject to the approximation that the system remains close to the limit cycle at all times during the course of its time evolution. At the limit cycle, the Hamiltonian H_0 takes the value v_0^2 where v_0 is the steady state velocity, $\left(\frac{\alpha}{\beta}\right)^{1/2}$.Close to the limit cycle, the Hamiltonian $H \simeq (v(t))^2 = \omega_0^2(x(t))^2$. The corresponding Fokker Planck equation in the energy space is,

$$\frac{\partial P_H}{\partial t} = D\frac{\partial}{\partial H}(HP_H) + (\gamma_H H - D)P_H \tag{8.9}$$

Here we define γ_H as $\gamma(v^2) \simeq \gamma_H\left(\frac{H}{m}\right)$ where m is the mass, taken to be unity here. The steady state zero current distribution is,

$$P_{steady}(H) = \mathcal{A}\exp\left[-\frac{1}{D_H}\int \gamma_H(H)dH\right] \tag{8.10}$$

In the case of the Rayleigh Helmholtz model we have $\gamma(v) = -a + bv^2$ where a and b are constants. Using the approximation that $H \simeq v^2$ we have

$$\gamma_H = b(H - H_0) \tag{8.11}$$

H_0 being the value of the total energy at the limit cycle, which is (a/b). Thus we find that the steady state,zero current distribution for this case as,

$$P_{steady}(H) = \mathcal{A}\exp\left[-\frac{b}{2D_H}(H - H_0)^2\right] \tag{8.12}$$

The Hamiltonian for the system under consideration is,

$$H = \frac{1}{2}\left(v^2 + \omega^2 x^2\right) \tag{8.13}$$

The steady state probability is therefore not separable in x and v, and we find it to be,

$$P_{steady}(x,v) = \mathcal{A}\left(e^{-\frac{b}{8D}v^4}\ e^{\frac{a}{2D}v^2}\right)\left(e^{-\frac{b}{8D}\omega^4x^4}\ e^{\frac{a}{2D}\omega^2x^2}\right)\left(e^{-\frac{b}{2D}\omega^2x^2v^2}\right) \tag{8.14}$$

We find the ratio of the steady state distributions at the initial and final points.

$$\frac{\tilde{p}_s(x,v_i)}{p_s(0,v_f)} = \exp\left(-\frac{\beta\nu}{2}\left[\left(\frac{v_f^4}{4} - \frac{v_i^4}{4}\right) - H_0(v_f^2 - v_i^2)\right]\right)\exp\left(-\frac{\beta\nu}{2}\left[\frac{1}{4}\omega^4x^4 - H_0^2\omega^2x^2\right]\right)\exp\left(\frac{-\beta\nu\omega^2x^2v_f^2}{2}\right)$$

Defining the change in the fluctuating entropy content from the initial to the final state, we have,

$$\Delta s/K_B = -ln[\tilde{p}_s(x, v_i)/p_s(0, v_f)]$$

Rearranging terms we have,

$$\frac{\Delta s}{K_B} = \frac{\beta}{2}\left[\frac{\nu}{4}\left\{(v_f^4 - v_i^4) + \omega^4 x^4\right\} - (\alpha-1)\omega^2 x^2 + \nu\omega^2 x^2 v_f^2\right] + \beta\left[\frac{\alpha(v_f^2 - v_i^2)}{2} - \frac{(v_f^2 - v_i^2)}{2}\right]$$

Using the definition of $H_0 = (\alpha - 1)/\nu$ we have for the last term,

$$\beta\left[\frac{a(v_f^2 - v_i^2)}{2\gamma} - \Delta E\right] = \beta\left[-\frac{\phi(v)}{\gamma} + \frac{b}{4\gamma}(v_f^4 - v_i^4) - \Delta E\right]$$

Thus, we finally obtain the expression for the fluctuating entropy as,

$$\frac{\Delta s}{K_B} = \frac{\beta}{2}\left[\frac{\nu}{4}\left\{(v_f^4 - v_i^4) + \omega^4 x^4\right\} - (\alpha-1)\omega^2 x^2 + \nu\omega^2 x^2 v_f^2\right] + \beta\left[-\frac{\phi(v)}{\gamma} + \frac{b}{4\gamma}(v_f^4 - v_i^4) - \Delta E\right] \tag{8.15}$$

8.2 The energy depot model

The phenomenon of self propulsion can also be modelled from the point of view of the energy depot. Here it is assumed that the particle is capable of taking up external energy and storing it in an internal energy depot. The energy of this depot can be used up either through internal dissipation or by converting some of this internal energy into kinetic energy.

Thus the energy balance equation for an internal energy depot e for a pumped Brownian particle can be given by,

$$\frac{de(t)}{dt} = q(\mathbf{r}) - ce(t) - h(\mathbf{v})e(t) \tag{8.16}$$

where $q(\mathbf{r})$ is the space dependent pump rate of energy, and $h(\mathbf{v})$ is the rate of conversion of internal energy to kinetic energy.

We choose,

$$q(\mathbf{r}) = q_0 \text{ and } h(\mathbf{v}) = d\mathbf{v}^2 \tag{8.17}$$

At the steady state, we find

$$e_0 = \frac{q_0}{c + d\mathbf{v}^2} \tag{8.18}$$

Thus the system is self propelled and this can be modelled using the velocity dependent potential $\psi(v) = +\gamma\frac{v^2}{2} - \left[-\frac{aq_0}{2d}ln\left(1 + \frac{dv^2}{c}\right)\right] - fv$ where f is a constant force acting upon the self propelled particle. We can write the corresponding Langevin equations in one dimension,

$$\dot{x} = v$$

$$\dot{v} = -\psi'(v) + \eta(t) \tag{8.19}$$

In the limit of small velocities this model gives back the Rayleigh Helmholtz model. The first law can be obtained as elaborated in the chapter 5, as

$$\Delta\left(\frac{1}{2}v^2\right) + \int dt\, v\frac{d}{dv}\left[-\frac{aq_0}{2d}ln\left(1 + \frac{dv^2}{c}\right)\right] = \int dt(-\gamma v + \eta) + \int v\, f \tag{8.20}$$

and we get $\Delta Q_m = -\int dt\, v\, \frac{aq_0 v}{c + dv^2}$

The various contributions to the entropy in equation (5.8) become

$$\Delta Q_{em} = \frac{f}{\gamma}\int dt\,\frac{aq_0 v}{c+dv^2} \tag{8.21}$$

$$\Delta Q_m = -\int dt\, v\,\frac{aq_0 v}{c+dv^2} \tag{8.22}$$

$$\Delta Q = \int dt(-\gamma v + \eta(t)) \tag{8.23}$$

The modified fluctuation dissipation relation can be written as,

$$\mu = \frac{1}{K_B T}\int_0^\infty dt\langle v(t)v(0)\rangle + \frac{1}{D_0}\int_0^\infty dt\left\langle \frac{v(t)}{c+dv(t)^2}\,v(0)\right\rangle - \frac{f_{const}}{D_0}\int_0^\infty dt\langle v(0)\rangle \tag{8.24}$$

8.3 The two dimensional Self Propelled particle

We now consider two spatial dimensions and consider particles with the heading unit vector $\mathbf{e}_h$ and the direction perpendicular to this in the velocity space is represented by the unit vector $\mathbf{e}_\phi$. Thus the time derivative of the velocity becomes,

$$\dot{\vec{v}} = \dot{v}\mathbf{e}_h + v\dot{\phi}\mathbf{e}_\phi$$

The corresponding Langevin equations can be written as,

$$\dot{v} = -\gamma v + \frac{\partial\Phi}{\partial v} + \eta_a(t) + \eta_p^h(t)$$

$$v\dot{\phi} = \eta_a(t) + \eta_p^\phi(t) \tag{8.25}$$

where the active and the passive noise is denoted by $\eta_a(t)$ and $\eta_p(t)$. The passive noise which is derived from the heat bath is of the form,

$$\eta_p^h(t) = \eta_x\cos\theta + \eta_y\sin\theta$$

$$\eta_p^\phi(t) = -\eta_x\sin\theta + \eta_y\cos\theta \tag{8.26}$$

where θ is the angular coordinate in the position space. The corresponding Fokker Planck equation can be written as,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial v}\left[\left(-\gamma v - \frac{\partial\Phi}{\partial v} + \frac{D_0}{v}\right)P\right] + (D_v + D_0)\frac{\partial^2 P}{\partial v^2} + \frac{D_\phi + D_0}{v^2}\frac{\partial^2 P}{\partial\phi^2} \tag{8.27}$$

where $D-0$ is the diffusion constant that arises from the passive noise correlation, i.e. from the Brownian heat bath, and D_v and D_ϕ are the diffusion constants that arise out of the active noise correlation, that is out of the fluctuations caused by the internal dynamics of the particles, in an artificial self propelled particle case, in the heading directions and the direction perpendicular to it, respectively. For a boundary at infinity, the steady state condition yields the distribution as follows,

$$P_{steady} = \exp\left[\frac{1}{D_v + D_0}\left(-\frac{1}{2}\gamma v^2 - \Phi(v)\right)\right]|v|^{\frac{D_0}{D_v+D_0}} \tag{8.28}$$

From the Langevin equation for the velocity coordinate, by using the method described, we arrive at the following form of the first law.

$$d\left(\frac{1}{2}\dot{x}^2\right) + \frac{d\phi}{dv}dx = \left[-\gamma\dot{x} + \eta_v^a(t) + \eta_p^h(t)\right]dx \tag{8.29}$$

The second term on the left hand side has the interpretation of the heat dissipated by the internal degrees of freedom and the right hand side of the heat given to the system, as before.

Considering the active and the passive noise to be delta function correlated individually, and hypothesizing that their cross correlation vanishes, it is possible to write a total noise term in the Langevin equation with an effective diffusion coefficient, $D_0 + D_i$ where i can be either v or ϕ. It is expected, then, that the transition probability of the forward and the reversed process would depend upon the gaussian function of this noise.

Proceeding in a manner similar to the one described in section 2 we get for the definition of entropy,

$$\Delta S = \Delta Q + \int_1^2 F_v dx - \frac{2}{D_v^{eff}} \Phi(v)|_1^2 + \frac{D_0}{D_v^{eff}} \Delta K + \ln v^{D_0/D_{eff}}|_1^2 \tag{8.30}$$

Defining $D_{eff} = D_0 + D_v$. If we assume that a small time dependent force is applied along the heading direction, our two dimensional problem becomes identical to the one dimensional problem described in the previous section and hence, the modified fluctuation dissipation relation becomes,

$$\mu = \left(\frac{D_0}{D_{eff}} \right) \frac{1}{K_B T} \int_0^\infty dt \langle v(t) v(0) \rangle + \frac{1}{D_v^{eff}} \int_0^\infty dt \left\langle \left(\frac{\partial \Phi}{\partial v} + \frac{D_0}{v} \right) \; v(0) \right\rangle \tag{8.31}$$

Chapter 9

Phase coexistence and the many body effect

Phase transitions are said to occur when the free energy of the system varies discontinuously across the transition. When the first derivative of the free energy varies discontinuously it is termed as a first order phase transition.The phenomenon of phase coexistence is nothing but a first order phase transition.[25]

9.1 Condition for phase coexistence

In a first order phase transition the coexisting phases have the same P and T. The condition for equilibrium is therefore that the total free energy is a minimum. The relative proportion of the two phases may vary but they are characterised by the Gibbs' potential per particle or rather, the chemical potential. Representing the Gibbs' potential per unit mass as $\mu_i(P,T)$ we have for the total Gibbs' potential,

$$G = m_1\mu_1 + m_2\mu_2 \tag{9.1}$$

where m_i is the mass of the phase i. The contributions from the two phases are additive as surface effects have been neglected. On transferring a small amount of mass from one phase to another at constant P and T, the condition for equilibrium is that the corresponding change in Gibbs' free energy should be zero, or rather the the Gibbs' free energy is a minimum with respect to mass transfer from one phase to another. Thus,

$$\delta G = \mu_1\delta m_1 + \mu_2\delta m_2 = 0 \tag{9.2}$$

The additional constraint imposed is that $\delta m_1 = -\delta m_2 = \delta m$. Therefore the condition for phase coexistence becomes,

$$\Delta\mu = \mu_1 - \mu_2 = 0 \tag{9.3}$$

This means that the two phases should have the same chemical potential to coexist at equilibrium. The derivatives of μ which give quantities such as specific volume or specific entropy are discontinuous across the phase boundary.

9.2 van der Waal's isotherm and critical exponents

The gas-liquid phase transition occurs due to intermolecular interactions. The simplest way to model this is by the van der Waal's equation of state,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{9.4}$$

The above equation is a cubic polynomial,

$$PV^3 - (bP + RT)V^2 + aV - ba = 0 \tag{9.5}$$

It has three roots, as can be seen on plotting the $P - V$ curve.

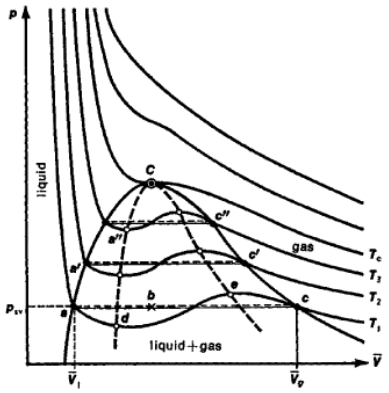


Figure 9.1: van der Waal's isotherms

These curves are known as the van der Waal's isotherms. In the region where the polynomial has three roots, it is seen that on increasing the temperature they move closer together until they finally merge at the critical temperature T_c. The corresponding critical volume V_c and critical pressure P_c can also be found. At the critical point,

$$(V - V_c)^3 = 0 \tag{9.6}$$

The critical volume, pressure and temperature are found to be,

$$\begin{aligned} V_c &= 3b \\ P_c &= \frac{a}{27b^2} \\ T_c &= \frac{8a}{27bR} \end{aligned} \tag{9.7}$$

Also it can be seen that while the van der Waal's isotherm is a monotonic function of V for $T > T_c$, there appears a kink in the graph below T_c indicating negative compressibility. This unphysical result arises only when the assumption of uniform density is used. The system actually undergoes a first order phase transition by breaking up into a mixture of phases of different densities. Using the Maxwell relation, $P = -(\partial A/\partial V)_T$ we find the area under the curve to be

$$A(V,T) = -\int_{isotherm} PdV \tag{9.8}$$

To compute this area we draw a horizontal line across the graph, and this is known as the Maxwell's construction.

The states a and c are defined by the conditions of equal pressure and the fact that they lie on a common tangent.

$$\begin{aligned} \frac{\partial A}{\partial V_a} &= \frac{\partial A}{\partial V_c} \\ \frac{A_2 - A_1}{V_2 - V_1} &= \frac{\partial A}{\partial V_c} \end{aligned} \tag{9.9}$$

As $(A_2 - A_1) = \Delta A = -\int_{isotherm} PdV$ we finally obtain,

$$\int_{V_a}^{V_c} PdV = P_a(V_c - V_a) \tag{9.10}$$

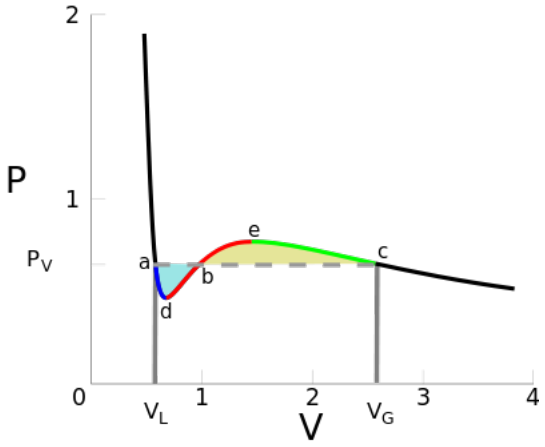


Figure 9.2: Maxwell's construction

9.3 Nucleation and spinodal decomposition

The Maxwell construction showed that in the transition region between a and c the system can lower its energy by breaking up into two mutually coexisting phases of different densities. The original van der Waal's isotherm in this region corresponds to an initial situation that is not in equilibrium. The system was prepared in a state of uniform density through rapid compression. The system needs time to break up into its equilibrium mixture, and the kinetics of the process depends on the compressibility or curvature of the free energy graph.

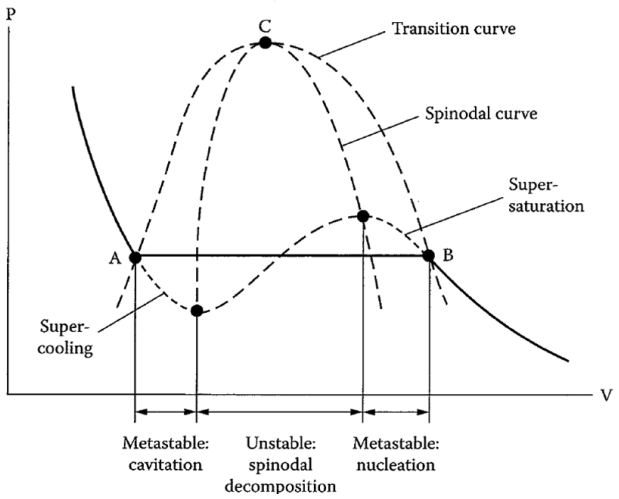


Figure 9.3: The van der waal's isotherm showing the transition region

When the compressibility is positive, that is, $(\partial P/\partial V) < 0$ the system is said to be in a metastable state. In this region the emergence of a new phase is triggered by nucleation. When the compressibility is negative, that is $(\partial P/\partial V) > 0$ the system is unstable and breaks up locally and spontaneously.This process is called spinodal decomposition. In the unstable region, the free energy has a negative curvature and the chemical potential which was previously defined as $-\frac{\delta F}{\delta n}$ in Chapter 2 now has a positive sign. Thus if a system can be prepared to be in this unstable region diffusion in the same direction as the concentration gradient, that is, from lower concentration to higher concentration would be observed.

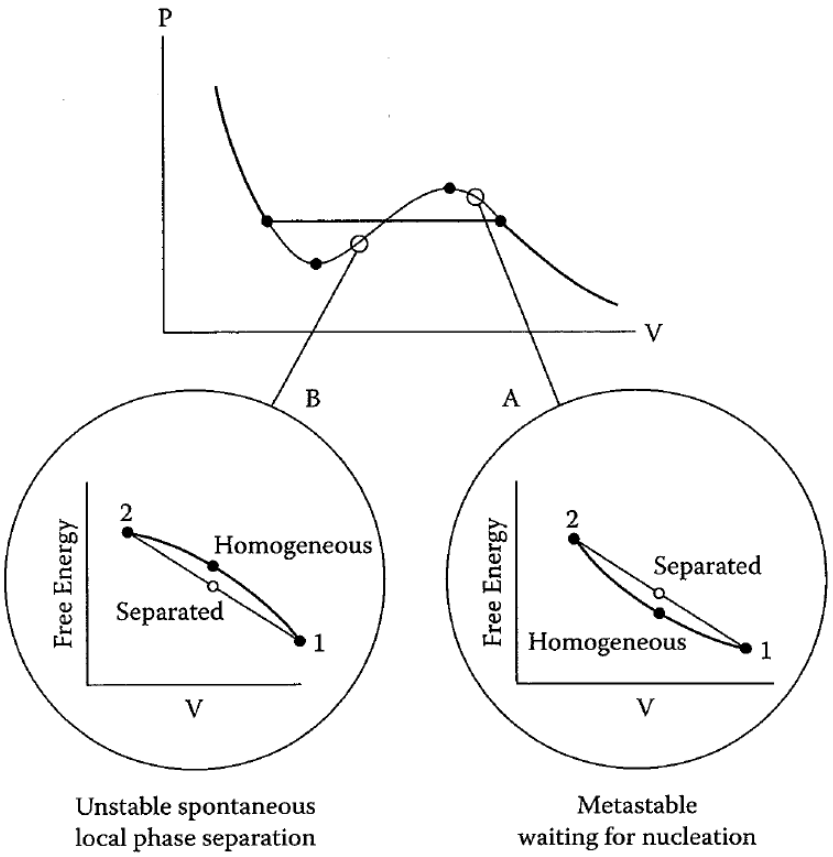


Figure 9.4: In region A the free energy has a positive curvature, the system is metastable and awaits the nucleation of a new phase.In region B, the free energy has negative curvature, the system is unstable and spontaneously phase separates locally

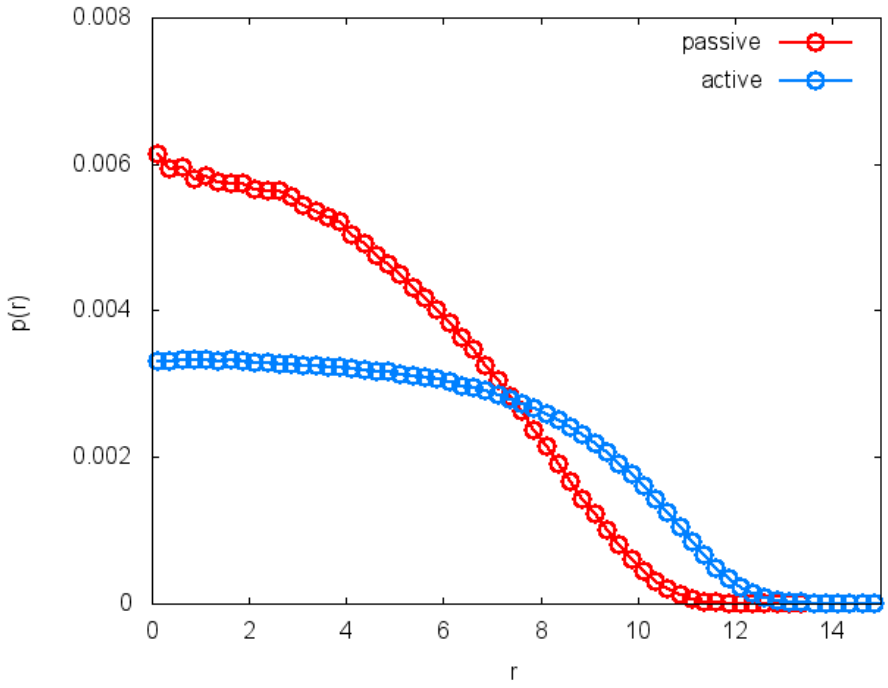
9.4 Non-equilibrium phase coexistence

While the above discussion is restricted is to equilibrium situations, it is interesting to consider extending the idea to self propelled many body systems. With this in mind, a system which had a number of interacting self propelled and passive particles in an external harmonic trap was considered.

The interaction potential was taken to be the WCA potential,

$$V(r) = 4\epsilon \left(\frac{1}{r^{12}} - \frac{1}{r^{6}} \right) \tag{9.11}$$

with the presence of a cutoff at the minima of this Lennard Jones' -like potential. For the purpose of calculation, $\epsilon = K_B T = 1$ is assumed and the probability distribution in position distribution was calculated. Thus we can see that the active particles have a longer tail of



the probability distribution, meaning that they are more favourably distributed towards the periphery. The passive particles tend to cluster towards the center of the trap. The active particles having a self propelling mechanism and the ability to transduce internal energy to kinetic energy and hence it seems likely that they would be able to cluster further away from the minima of the harmonic potential well.

These are two species which interact and occupy different positions in the potential trap, with different densities of clustering. This is the first indication of a non-equilibrium phase co-existence occurring in this system. Further investigation is required to determine the exact character of this phase coexistence as well as to determine local structure and composition.

Chapter 10

Conclusion and Outlook

In this project, I have described a formulation of fluctuating thermodynamics for the self propelled system. Thus I have been able to identify the energy conservation equation. The terms in the non-equilibrium entropy have also been identified. In the context of linear response theory, the modified fluctuation theorem has also been calculated and the possibility of defining an effective temperature has been ruled out. Using this formalism, models of experimental and biological significance such as the Rayleigh Helmholtz model and the energy depot models of self propulsion have been considered, and the first and second law of thermodynamics have been shown, with the fluctuating entropy being calculated explicitly. Using an approximation of the system being around a limit cycle, the steady state and the fluctuating entropy content for a Rayleigh Helmholtz model in a harmonic trap has also been calculated. An attempt has been made to generalise to higher dimensions,and within this formalism, the two dimensional self propelled particle has been considered.

Finally the interacting many body problem of a mixture of self propelled and passive particles placed in a harmonic trap has been considered. As the self propelled particles showed a tendency of clustering towards the periphery of the trap, and the passive particles toward clustering in the centre of the trap, the first signatures of a possible phase coexistence were found.

We hope to extend this formalism for an active Brownian particle in three dimensions. We also hope to investigate the many body problem and discover local clustering, structure and also to characterise this phase coexistence.

Bibliography

[1] Becco, C., N. Vandewalle, J. Delcourt, and P. Poncin (2006),Physica A **367**, 487.

[2] Cavagna, A., A. Cimarelli, I. Giardina, G. Parisi, R. Santagati,F. Stefanini, and M. Viale (2010), Proceeding of the National Academy of Sciences of the United States of America **107**, 11865.

[3] Cisneros, L. H., R. Cortez, C. Dombrowski, R. E. Goldstein, and J. O. Kessler (2007), Experiments in Fluids **43**, 737

[4] Bazazi, S., J. Buhl, J. J. Hale, M. L. Anstey, G. A. Sword,S. J. Simpson, and I. D. Couzin (2008), Current Biology **18**,735

[5] Ibele, M., T. E. Mallouk, and A. Sen (2009), Angewandte Chemie International Edition **48**, 3308.

[6] Blair, D. L., T. Neicu, and A. Kudrolli (2003), Physical Review E **67**, 031303.

[7] Kudrolli, A., G. Lumay, D. Volfson, and L. S. Tsimring (2008), Physical Review Letters **100**, 058001.

[8] Vicsek, T., A. Czirok, E. Ben-Jacob, I. C. I, and O. Shochet(1995), Physical Review Letters **75**, 1226.

[9] Debasish Chaudhuri, Abhishek Chaudhuri (2012), Physical Review E **85**,021102

[10] Robert Zwanzig, Nonequilibrium Statistical Mechanics

[11] Jarzynski.C. Physical Review Letters(1997) **78**, 14.

[12] Crooks,G.E. arXiv:cond-mat/9901352v4[cond-mat.stat-mech] 29 July 1999

[13] U.Marconi, A.Puglisi, L.Rondoni and A.Vulpiani,Physics Reports **461**,111 (2008)

[14] P.Hänggi,H.Thomas,Phys Rep **88**,207, (1982)

[15] P.Martin, A.J.Hudspeth and F. Jülicher, Proc. Natl.Acad.Sci. USA **98**, 14380,(2001)

[16] A.Crisanti, F.Ritort J.Phys.A:Math. Gen. **36**, R181,(2003)

[17] T.Speck and U.Seifert, Physical Review E **79** 04012(R) (2009)

[18] J.Prost, J.-F.Joanny,J.M.R.Parrondo, Phys. Rev. Lett. **103** 090601 (2009)

[19] U.Seifert and T.Speck Europhysics Letters **89**, 10007(2010)

[20] A.Sarracino, D.Villamaina, G.Gradenigo and A.Puglisi,**92** 34001 (2010)

[21] G.Verley, K.Mallick and D.Lacoste Europhysics Letters **93**, 10002 (2011)

[22] Schimansky-Geier L., Ebeling Werner, Erdmann Udo (2005), Acta Physica Polonica B **36**,5

[23] Wong,Wolymes PNAS **108** pp 1184 (2011)

[24] Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences (2nd ed) by C.W.Gardiner

[25] Introduction to Statistical Physics (2nd edition) by Kerson Huang

[26] Principles of Condensed matter physics, P.M.Chaikin and T.C.Lubesnky

[27] H.Risken *The Fokker Planck equation:Methods of solutions and applications*(Springer-Verlag,Berlin,1989)

[28] G.S.Agarwal,Zeitschrift für Physik **252**,25 (1972)